AFIT/GEE/ENV/94S-08

DEVELOPMENT OF FIELD GUIDANCE FOR ASSESSING FEASIBILITY OF INTRINSIC BIOREMEDIATION TO RESTORE PETROLEUM-CONTAMINATED SOILS

THESIS

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AFIT/GEE/ENV/94S-08

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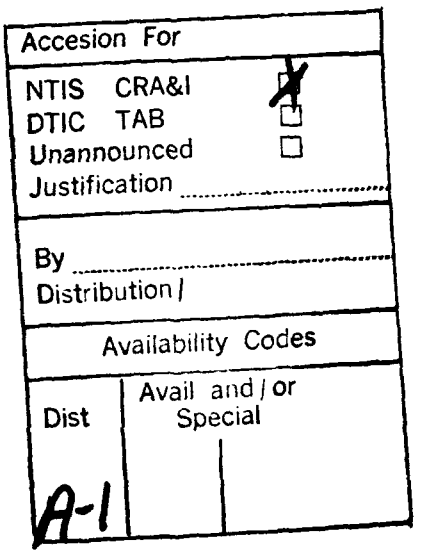

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THESIS

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Abstract

This research evaluated the process of intrinsic bioremediation, also called natural attenuation, and the parameters that affected it. The goal of this study was to use these intrinsic bioremediation parameters to develop a valid prediction of the cleanup duration using this restoration technology. This analysis was limited to a JP-4 release and focused on the remediation of the BTEX constituents to a cleanup level of 10 ppm total BTEX.

The review of intrinsic bioremediation found that the BTEX hydrocarbons can aerobically and anaerobically biodegrade. Of the many factors that affect intrinsic bioremediation, those that most influenced its occurrence were the quantities of aerobic and anaerobic electron acceptors used in biodegradation. The electron acceptors considered in this research were oxygen, nitrate, manganese (IV), iron (III), and sulfate.

A no-dispersion biodegradation model was developed to determine the prediction of the intrinsic bioremediation duration based on the concentrations of individual electron acceptors. Only the aerobic electron acceptor had a measurable influence on the biodegradation model; hence, the prediction results focused on the aerobic biodegradation and its boundary with the anaerobic portion.

The key factors used to characterize this boundary and its movement was the initial quantities of BTEX, dissolved oxygen and the relative velocity of the ground water moving through the retarded plume. A linear regression was performed to relate the three parameters mentioned above to the motion of the aerobic boundary.

With future validation of this regression data, this information may be used by Air Force site managers to predict the time aerobic intrinsic bioremediation can restore a plume of a given size. Knowing the possible cleanup duration is preliminary to determining how feasible intrinsic bioremediation may be at a particular site.

DEVELOPMENT OF FIELD GUIDANCE FOR ASSESSING FEASIBILITY OF INTRINSIC BIOREMEDIATION TO RESTORE PETROLEUM-CONTAMINATED SOILS

I. Introduction

General Issue

The Air Force is determined to comply with environmental laws while operating and maintaining a viable fighting force. In the daily operations of this organization, substance releases into the soil and ground water have impacted the environment. Specifically, spills of petroleum products at Air Force installations, especially fuels, have resulted in numerous ground water and soil contamination sites.

The Air Force is now challenged to remediate these release sites to comply with Federal and State laws and reduce the potential hazards to human health and the environment. It is this potential risk to human health and environment caused by contamination that motivates the remediation effort and clean-up standards. Each of these contaminated sites will usually necessitate a costly study and corrective action. Air Force environmental managers must use effective remediation methods with limited resources in order to address the host of impacted sites.

The goal in the restoration of these sites is to reduce certain contaminant concentrations within a finite amount of time or at least a finite distance from the source. This will protect potential recipients of the contamination from health risk. Contamination can reside in the soil or be dissolved in the ground water. Many methods have been and are being developed to reduce levels of these contaminants. A significant difference between these remediation methods is the amount of resources and capital required to execute them effectively. High expense methods include removal of all

contaminated soil from the site and treating elsewhere or pumping and treating the ground water from the site over a considerable length of time.

Specific Problem

The funds available to accomplish remediation work are limited, especially considering federal tax dollars and the likely decrease in their availability. There are too many sites, especially in Department of Defense (DoD) and the Air Force, that require attention compared to the funds needed to address all of the sites by conventional methods. Remediation methods must be developed that are low cost and applicable to many remediation sites if protection of human health and environment is to be a reality.

One method of ground water restoration in particular holds a promise of effective remediation while requiring less capital than other methods. This method is intrinsic bioremediation, also called natural attenuation. It involves using microbial biodegradation to remove the contaminant and monitoring this process until completion. The term intrinsic is used because the microorganisms considered for the biodegradation are those indigenous to the area. With adequate study of and practical instruction on the aspects of intrinsic bioremediation, this ground water restoration technology may be made available to managers of existing ground water contamination sites. Hopefully intrinsic bioremediation can be considered and utilized as the definitive remediation method at many of these sites.

Objective

This thesis will address the method of intrinsic bioremediation and the parameters of the soil and contaminant that most affect the process. The only scenario considered will be fuel contamination and the intrinsic bioremediation of the hazardous constituents. The plan for this research is to develop a relationship between the parameters that will

allow prediction of the duration of intrinsic bioremediation. This duration will be defined as the time needed to reduce the hazardous constituents of fuel to an acceptable clean up level as applied to a typical ground water restoration site. This prediction is intended to be an initial, yet straightforward assessment of using intrinsic bioremediation at a restoration site. The parameters used as inputs to this success forecast will be derived from specific site data that can be obtained from a preliminary site investigation.

Procedures will be outlined to allow compilation of this site data into a simple forecasting model that is designed to be usable for a base environmental manager at a restoration site. The forecast will indicate the time that may be required to bring the contaminants to a certain clean-up standard. The site manager can use this time estimate to determine the possible extent the plume will travel. Considering these factors along with subjective criteria, the manager can judge whether conditions are favorable or unfavorable for intrinsic bioremediation to successfully restore the site. If the conclusion is favorable, then the manager has evidence to support the full assessment of the site in order to demonstrate that intrinsic bioremediation is occurring. If the conclusion is not favorable, then the manager may have an indication as to the reason it is not favorable which may assist the manager in deciding what corrective action is suitable for the site.

Once an environmental manager decides that conditions are favorable for intrinsic bioremediation to be successful, a full site assessment can be accomplished to establish the potential efficacy of intrinsic bioremediation to the satisfaction of regulators. This full characterization of a site will likely need to demonstrate active biodegradation and measure the actual rates of hydrocarbon decay. The Air Force Center for Environmental Excellence (AFCEE), Brooks AFB, TX, is currently developing a protocol for accomplishing such a site assessment.

Two immediate benefits may result from applying this research as described above. First, by obtaining a preliminary indication of favorable conditions for intrinsic

bioremediation, the site manager has supportive evidence to promote full characterization to regulators in terms of the extra time required and DoD funding sources for the approval of resources.

A second possible benefit exists if the site is in a location where regulated standards may be undefined, especially at some overseas DoD installations. Determining that intrinsic bioremediation may restore the site within favorable limits may be satisfactory evidence for the DoD executive agent to initially approve intrinsic bioremediation as the restoration action.

The intended long-term benefit of this research effort is that it result in a usable model that will allow remediation site managers to consider intrinsic bioremediation for their site. As more managers investigate intrinsic bioremediation, more opportunities to prove the feasibility and success of this remediation method will be realized. The outcome should be an increase in the use of intrinsic bioremediation as the action selected to restore contaminated sites. The consequent savings of restoration funds by using intrinsic bioremediation where it is feasible can then be applied to other sites where more intensive remediation alternatives are needed.

Scope and Limitations

This thesis will only consider a JP-4 release to the subsurface with a study of the intrinsic bioremediation in the ground water at the release site. Therefore, the typical hydrocarbons contained in JP-4 are the only contaminants considered for remediation. This research will ignore remediation of the contaminated unsaturated soil as volatilization of fuel constituents is the primary exposure pathway and will not likely affect populations located off installations. The exposure due to migration of contaminated ground water has more potential to affect adjacent populations, therefore this thesis will focus on ground water remediation only. This analysis of intrinsic

bioremediation will also be limited to the contaminants that pose the highest risk to human health and the environment as noted in the literature.

JP-4 was chosen as the sole pollution source as it is well characterized compared to other fuels and it is a common pollutant on Air Force installations. Also, limiting the pollutants considered will provide a methodology that is relatively easy to follow. Other fuels should be able to be examined in the same way through future thesis work or adapting common aspects of other fuels to this JP-4 analysis.

II. Literature Review

Overview

Intrinsic bioremediation has gained attention from researchers as a possible remediation method for ground water contamination. Many investigators in the field of remediation believe that in some cases intrinsic bioremediation can be used to restore a contaminated site within a reasonable amount of time and within acceptable human health and environmental risk levels.

Lt Col Ross Miller, Chief of the Technology Transfer Division of AFCEE, has extensively promoted the topic of intrinsic bioremediation as a feasible means of remediating some Air Force contamination sites. His premise is that the Air Force is spending huge sums of money remediating ground water systems and yet some contamination sites could be restored effectively with intrinsic bioremediation. The cost savings are easily apparent. Obtaining an adequate site characterization and monitoring the progress of the intrinsic bioremediation effort are the only substantial expenses. By comparison, the installation of one pump and treat system could cost between $1M to $5M dollars (Miller, 1992: 3). When compared to the costly installation, operation and maintenance of a pump and treat system, a successful intrinsic bioremediation process is an efficient use of limited financial resources.

Intrinsic bioremediation relies primarily on microorganism biodegradation to remediate the pollutants by chemical conversion. The concentrations of pollutants are reduced by dispersion of the plume as well, but that influence will not be considered in this work.

This literature review will investigate intrinsic bioremediation and specifically the hydrocarbon biodegradation process with its application to JP-4 and contaminants of primary interest. Next, this work will present data on the theoretical and observed

feasibility of hydrocarbon biodegradation. Lastly, the parameters that influence intrinsic bioremediation will be reviewed along with a detailed look at a key factor in the process, the influence of the electron acceptors.

Hydrocarbon Plume Profile

Basic View. The spill of petroleum into the subsurface results in the petroleum migrating to the water table and accumulating there. Petroleum products are considered non-aqueous phase liquids (NAPLs) because they will not readily dissolve into the ground water. Because the specific gravities of petroleum fuel are less than 1.0, these NAPLs will remain above the water table. However, a few contaminants dissolve into the ground water and create a hydrocarbon plume moving in the direction of ground water flow. A diagram of such a petroleum release is shown below with the ground water moving from left to right.

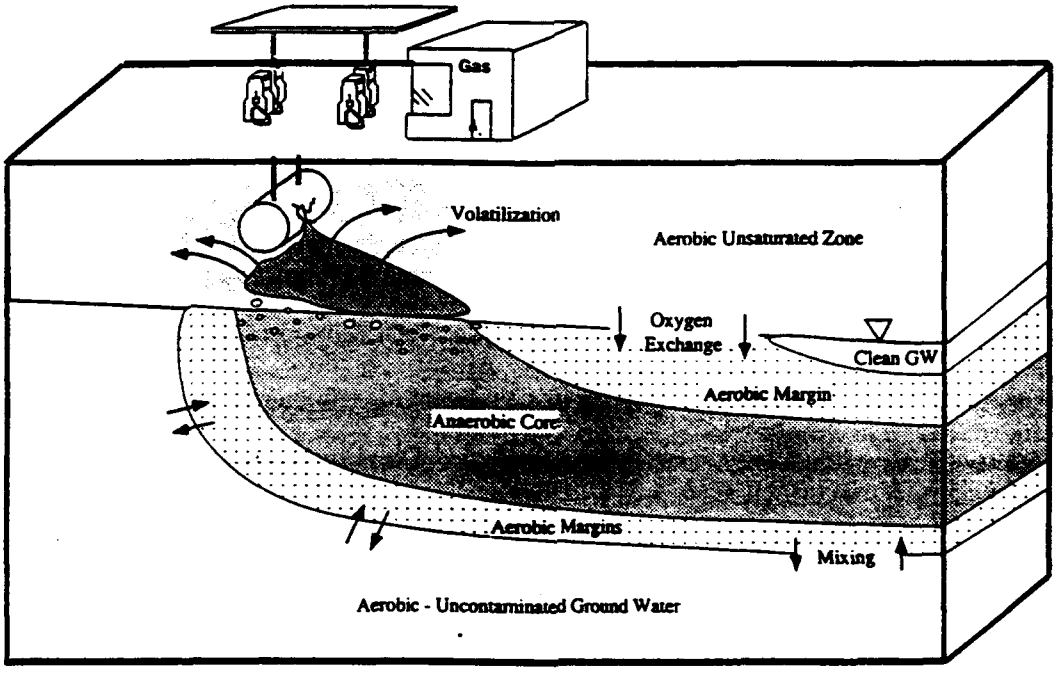

Figure 1. Basic View of Hydrocarbon Plume from a Fuel Release. (Borden, 1994: 184)

Figure 1 also shows the partitions of the plume that are generally aerobic or anaerobic. These partitions have been defined even further as described in the following section.

Detailed View. Observing a hydrocarbon plume in more detail, we see portions of the plume that have characteristics other than just aerobic or anaerobic. A plume in Bemidji, MN, resulted from a crude oil release and was studied by the U.S. Geological Survey. The researchers portion the plume according its position relative to the NAPL and the presence of oxygen (oxic conditions) or absence of oxygen (anoxic). In this plume they found five zones or portions describing the makeup of the plume. The plume is represented here.

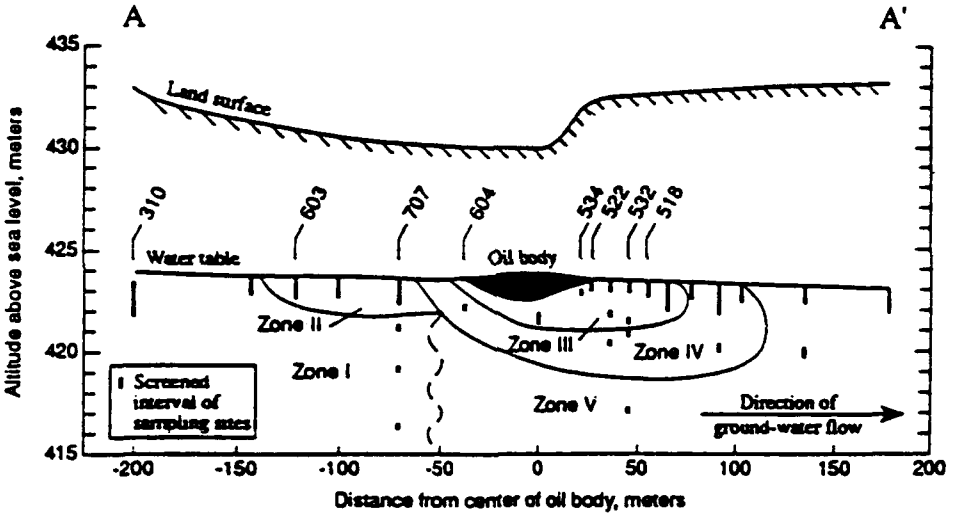

Figure 2. Detailed View of Intrinsic Bioremediation Zones Within Hydrocarbon Plume, Bemidji, MN. (Baedecker, 1993: 573)

Zone I is the native ground water (oxic). Zone II is contamination from additional crude oil release which may or may not exist at a site. Zone III is the concentrated dissolved contaminant plume (anoxic). Zone IV is a transition zone between the concentrated plume and the surrounding native water which is suboxic. Lastly, they show the oxic ground water downgradient of the NAPL in Zone V. The activity of intrinsic

bioremediation in the oxic zones will be aerobic biodegradation and the anoxic zone will see anaerobic biodegradation occurring.

The Hydrocarbon Biodegradation Process

Hydrocarbon biodegradation is the breakdown of hydrocarbons through the action of microbes. The hydrocarbons are converted into new compounds which are usually less harmful (Reinhard, 1994: 131). A common product of hydrocarbon biodegradation is carbon dioxide. Microorganisms metabolize the contaminants using electron acceptors. Chemically, the contaminant molecule is oxidized and the electron acceptors are reduced. The electron acceptor is any compound that is able to be reduced with microorganisms as the catalyst. Those compounds that have observed potential as electron acceptors will be considered in this work.

Aerobic Biodegradation. Oxygen is the electron acceptor used by the aerobic microbes in biodegradation of contaminants. The oxygen in the unsaturated soil (vadose zone) dissolves in the ground water and is available to microorganisms for use in biodegradation. Aerobic biodegradation usually occurs at a faster rate and before any anaerobic biodegradation. Once oxygen is depleted in a portion of ground water by aerobic biodegradation, reaeration will occur as oxygen in the vadose zone dissolves in the ground water. However, the influence of reaeration on sustaining aerobic biodegradation is uncertain (Wilson, 1994). The upper portion of the aquifer receives new oxygen, but, as Figure 1 shows, the core of a plume is usually a measurable distance down into the aquifer. There is a margin of aerobic biodegradation occurring, yet reaeration will likely not influence the degradation of the plume core.

The aerobic degradation of hydrocarbons can be modeled as a first order exponential decay relationship (Domenico and Schwartz, 1990:476). The aerobic decay half-lives for contaminants vary according to the microbial conditions at a given site.

Published range values or observed values for the unacclimated half-lives of some key compounds of interest are shown in Table 1.

Table 1. Aerobic Biodegradation Half-Lives

(MacKay, 1993: 64-82; Howard, 1991: 111; Vashinav and Babeu, 1987: 242)

Hydrocarbons	Half-lives (hours)
benzene	240-384, 672
toluene	168-672
ethylbenzene	144-240, 888
xylenes (ortho-, meta-, para-)	168-672

The reasons these are compounds of interest is discussed on page 12. It is worth noting that for benzene and ethylbenzene, literature suggests that the half-lives should be much greater than toluene or xylene. Therefore, the upper bound of decay constants for benzene and ethylbenzene used for this research will be higher than these values in order to ensure an accurate yet conservative analysis.

Anaerobic Biodegradation. Anaerobic microorganisms use electron acceptors other than oxygen to metabolize hydrocarbons. These electron acceptors include chemical species of nitrate, sulfate, manganese (IV), iron (III), and even carbon dioxide (Reinhard, 1994:131). Nitrate, sulfate, and carbon dioxide are soluble in water and will move in accord with the ground water. Manganese (IV) and iron (III) are insoluble in water as a rule and will be found in the solid phase of the soil matrix. The products of anaerobic biodegradation differ for each acceptor used. Microorganisms that use one type of anaerobic electron acceptor may not be acclimated to use another.

The anaerobic decay is a first-order exponential function also. Observed anaerobic half-lives are shown in Table 2 for a few contaminants.

Table 2. Anaerobic Biodegradation Half-Lives

(MacKay, 1993: 64-82; Howard, 1991):

Hydrocarbons:	Half-Lives: (hours)
benzene	2688-17280
toluene	1344-5040
ethylbenzene	4224-5472
o-xylene	4320-8640
m-xylene	672-12688
p-xylene	672-2688

Because the literature only provides a generic range of anaerobic half-lives for these contaminants, the anaerobic constants in this research will be the same for all anaerobic biodegradation regardless of the electron acceptor used.

Redox: The Energy in the Process. Biodegradation, whether aerobic or anaerobic, is an oxidation-reduction or redox reaction. Microbes utilize the redox energy potential from the biodegradation reactions to metabolize their fuel and to produce biomass. From a geochemical viewpoint, we can consider the microbes as the catalyst in the redox reaction of organic contaminants and electron acceptors resulting in products such as carbon dioxide and water. According to the figure shown, each reaction of an electron acceptor offers a different energy potential to microorganisms.

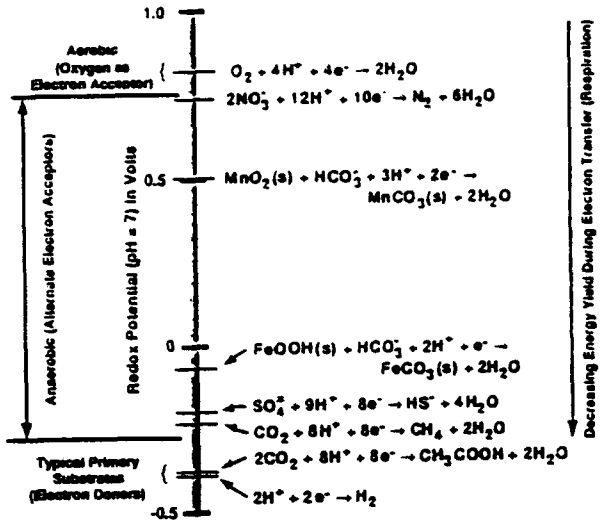

Figure 3. Key electron acceptors in the intrinsic bioremediation oxidation/reduction reactions. Redox potentials are from Stumm and Morgan as reported by Bouwer (Bouwer, 1994:151).

We observe a defined hierarchy of electron acceptors according to energy yield. Oxygen yields the highest redox energy of all reactions. The reactions turn anaerobic when oxygen is depleted and the order of energy potential is nitrate, manganese (IV), iron (III), sulfate and carbon dioxide. The individual reactions for the BTEX compounds combined with the respective electron acceptors is shown in the section titled: "Electron Acceptors and BTEX Biodegradation".

Contaminants of Interest. The primary concern over petroleum releases to the ground is the hazard to human health and the environment. Several constituents of petroleum are considered to pose a measurable risk to human health when consumed. Those appraised to be of most concern are aromatic compounds known as the BTEX compounds: benzene, toluene, ethylbenzene, and xylene isomers (ortho, meta, and para). Specifically, benzene is a class A carcinogen by EPA standards. The BTEX compounds are found in most fuel mixtures. Fuel such as JP-4 typically contains less BTEX constituents than gasoline, but more than diesel.

Many constituents of petroleum fuels are not as well characterized as the BTEX compounds in regard to their toxicity potential. Yet, nearly all of the literature indicates that these aromatic compounds should be the most hazardous or pose the most health risk of the organic compounds found in petroleum. Therefore, this effort will focus on the intrinsic bioremediation effect on the BTEX constituents as they are the components of interest from a risk management perspective.

A key question of any intrinsic bioremediation effort is to what level the BTEX compounds, or any remaining contaminants, must decrease in order for the aquifer to be considered clean. The thesis written by Blaisdell and Smallwood (GEE-93S) investigates the various cleanup standards that states have established. These standards are based on total BTEX concentration, individual constituent concentrations, and/or total petroleum hydrocarbons (TPH). The standards are usually adjusted according to the petroleum product that generated the contamination (e.g. gasoline). Examples of standard values established were: 100 ppm TPH; 10, 20 or 100 ppm total BTEX and .5, .01 and .005 ppm Benzene. The most common standard for states that use a total BTEX cleanup standard is 10 ppm (Blaidell and Smallwood, 1993: 90). This value will constitute the cleanup level for use in this thesis.

Feasibility of Hydrocarbon Biodegradation

Since the BTEX constituents are of interest, it must be established that microorganisms can biodegrade the BTEX compounds. This section will discuss this question first by reviewing the geochemical potential for biodegradation. Second, the author will present evidence from field observations that indicate the loss of the BTEX compounds via biodegradation. In both cases, the aerobic and anaerobic pathways will be investigated.

Premise for BTEX Biodegradation. The first question with regard to a theoretical premise for biodegradation is the existence of subsurface microorganisms. The population of microbes in soil and ground water is expected to be around 10^6 to 10^7 cells/g of dry soil (Lee and others, 1988: 30). This estimate was derived from samples taken from an uncontaminated shallow aquifer.

The second question to support a theoretical basis of biodegradation is the chemical feasibility. According to Chapelle (1993), microorganisms have a number of possible and likely pathways for degrading aromatic hydrocarbons. Researchers have studied *Pseudomonas* bacteria especially and have shown their potential to degrade aromatic hydrocarbons. Other strains of bacteria such as *Acinetobacter* and *Bacillus* also exhibit this potential. The number of organisms and the presence of the associated enzyme systems affect the rate of biodegradation of benzene as well as the other BTEX compounds (Chapelle, 1993:336-337).

Chapelle discusses aerobic and anaerobic degradation of the aromatic hydrocarbons and describes possible pathways for each BTEX compound. The diagram that follows illustrates a pathway of aerobic biodegradation of benzene.

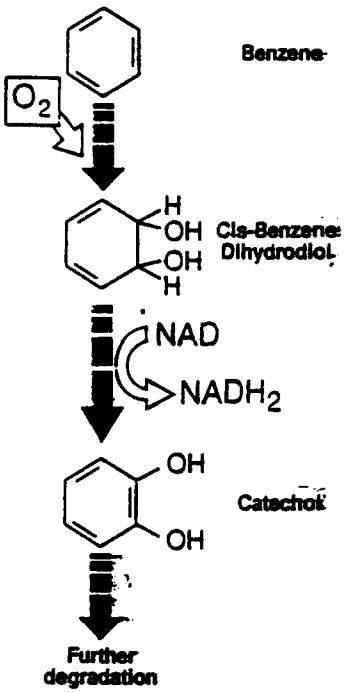

Figure 4. Example of aerobic biodegradation pathway of benzene to catechol. (Chapelle, 1993: 337)

For benzene to anaerobically degrade, its ring must first be oxidized or reduced. Toluene has a number of possible degradation pathways, especially in the presence of Fe(III) (Chapelle, 1993:342-343). The presence of nitrate allows all four BTEX compounds to anaerobically degrade and the decay rates are noted as significant (Chapelle, 1993:344).

Observed Biodegradation. Numerous studies and experiments have observed actual degradation of petroleum/fuels by microorganisms. An experimental observation of aromatic compounds in 1981 demonstrated the ability of these compounds to degrade. Benzene, ethylbenzene and toluene were characterized as experiencing significant degradation with rapid adaptation (Tabak and others, 1981:1509). An experiment with *Pseudomonas pickettii* demonstrated measurable growth of the microbes with benzene, toluene and ethylbenzene (Kukor and Olsen, 1990:416).

Other laboratory studies show evidence that all BTEX compounds are degraded despite the lack of oxygen. In 1988, under denitrifying conditions and a 62 day incubation, benzene, toluene, o- and m-xylene experienced a 34, 35, 27, and 41% reduction (Chapelle, 1993:344). With a sulfate-reducing system, toluene was the substrate of choice and the xylenes next. Benzene began to degrade in the absence of other aromatics.

A significant field investigation of aerobic and anaerobic biodegradation was conducted in Bemidji, Minnesota at a crude oil spill site (Bennett and others, 1993; Eganhouse and others, 1993; Baedecker and others, 1993). The plume constituents were characterized along with the local hydrogeology. Definite gradients were observed in dissolved oxygen and other electron acceptor concentrations between the native ground water and the boundary of the contamination. A measured decrease in volatile dissolved organic compounds was also observed along this boundary that was beyond what would be expected from sorption or dispersion. These researchers concluded that aerobic and anaerobic biodegradation was reducing the mass of organic materials in the ground water. Key evidence was that the expected dispersion of the plume was not observed and this mass of dispersed contaminants was converted through biodegradation.

Other field investigations of aerobic biodegradation include a 1990 study at a fuel storage area within a naval air station located in Maryland (Lee and Hoeppel, 1990). Contamination was found over 5 hectares with a 4 m depth. Samples taken from surface soil near recent spill sites detected BTEX compounds. At a similar spill, yet occurring some time before, little of the original fuel constituents were detected. In particular, benzene was absent and toluene found at very low levels. This decrease could be attributed only to natural processes.

Hinchee and Say compiled results from eight sites where jet fuel contaminated the subsurface. In situ respiration tests were conducted to measure the oxygen consumption

over time in a bioventing scenario. Oxygen levels declined to 10% of their original values over 80 hours. Since background levels of oxygen declined by a maximum of 2% over the same time, aerobic biodegradation was the cause for the significant oxygen decline (Hinchee and Say, 1992: 1309).

In regard to anaerobic processes of biodegradation, a study was completed on this process at a gasoline contamination site near Empire, Michigan (Barlaz and others, 1992). A site characterization was done to include a soil gas survey and vertical coring. The dissolved O2 in the aquifer was low enough to consider the region anaerobic. The researchers computed first order biotransformation rates for the BTEX compounds in the aquifer and presented those results. Toluene degraded the fastest followed by ethylbenzene and the xylenes. Benzene showed no apparent anaerobic biodegradation in this study.

To summarize, aerobic and anaerobic biodegradation of the BTEX compounds can occur. Anaerobic decay of benzene seems to be the slowest of all reactions and may not occur at all sites. We see that aerobic decay as a rule is faster than anaerobic decay and anaerobic processes won't initiate until oxygen is depleted from a plume. An unanswered question remains for the possible rate differences between the various anaerobic reactions. Though it is likely that the microbes are different in anaerobic biodegradation using different electron acceptors, the difference in anaerobic decay constants is uncertain.

Parameters that Influence Intrinsic Bioremediation

Electron Acceptor Availability. As referred to earlier, the quantity of electron acceptors in the aquifer is considered a primary determinant of the potential for hydrocarbon biodegradation. Their respective quantities probably affect biodegradation rates along with the quantity of the contaminant. The hierarchy of which electron

acceptor is used depends on the redox energy potential that the electron acceptor can provide in accordance with the presence of acclimated indigenous microorganisms.

Acclimated Microorganisms. Two things are important when considering the microbe population. The first consideration is the presence of native microorganisms that are acclimated to using aromatic hydrocarbons as fuel. Secondly, if they are anaerobic microorganisms, they must able to use one of the available anaerobic electron acceptors in biodegradation. There is normally a lag time involved which is the time needed for the microbes to acclimate to hydrocarbons or available electron acceptors in the aquifer prior to biodegradation. Observed lag times are not readily available, however a sample value was published for a 43 day lag time for sulfate reducing bacteria to acclimate to m-cresol (Chapelle, 1993:346).

Random field investigations indicate that it is viable that some indigenous aerobic microorganisms can biodegrade aromatic hydrocarbons. Native anaerobic microbes follow this same expectation, yet there may be some additional lag time observed.

Hydrogeologic Factors. In addition to the decay processes themselves, there are other processes that will influence the attenuation of fuels in ground water. The natural dispersion of the contaminant plume caused by ground water motion will cause the concentration to drop as the constituents disperse with water flow and traverse to water flow. Advection will move the contaminant mass away from the source but sorption to soil particles will slow this movement of the contaminants. Advection and dispersion are functions of the aquifer characteristics defined by the ground water velocity, porosity and dispersivity.

The retardation factor is a key parameter affecting the actual advective velocity of the plume. The retardation factor is the value of the linear velocity of the ground water divided by the velocity of the contaminant. The factor is a function of the porosity, solids density and distribution coefficient. The distribution coefficient, in turn, is a function of

the contaminant's partition coefficient between organic carbon and water and of the soils' organic fraction. The partition coefficient is empirically correlated with the octanol/water partition coefficient. The retardation equation is found in Chapter III, page 34.

Other parameters may affect biodegradation at a site. Two in particular are pH and water hardness which may hinder biodegradation if they are beyond a range of ideal conditions. The ideal range for pH values are 6.5 to 7.5. Water hardness of approximately 100 mg/L (based on CaCO3) is best for biodegradation (Wilson, 1994).

Electron Acceptors and BTEX Biodegradation

In this section, the relationship of the BTEX compounds and the electron acceptors will be studied in more depth. Specific information on each acceptor and the stoichiometric relation to each contaminant of interest will be presented. These relationships are an uncomplicated description of the reactants and end products of intrinsic bioremediation. Before these reactant/end product relationships are discussed, this paper will present a brief account of other organic compounds observed in the hydrocarbon biodegradation process.

Interim Products of BTEX Biodegradation. Biodegradation is an iterative chemical process that produces various organic species. An interim product from benzene aerobic decay is catechol (Gottschalk, 1986:159). Toluene decay may produce metacatechol while xylene and ethylbenzene may see dimethylcatechol. Anaerobic decay of benzene may produce phenol, cyclohexane and aliphatic acids. Toluene decay could produce benzyl alcohol benzoic acid and benzoate (Chapelle, 1993, 337-343). In short, each biodegradation pathway consists of many iterative decay actions before the end product is realized. This work will limit its consideration to the BTEX compounds and end products only.

Oxygen. As discussed, the use of oxygen by aerobic microorganisms provides the most redox energy when compared to other biodegradation reactions. Thus, assuming the presence of aerobic microbes, oxygen will then be the first electron acceptor utilized in intrinsic bioremediation. The observed biodegradation stoichiometric reactions are shown:

Benzene: $C_6H_6 + 7.5\ O_2 \Rightarrow 6\ CO_2 + 3\ H_2O$

Toluene: $C_7H_8 + 9\ O_2 \Rightarrow 7\ CO_2 + 4\ H_2O$

Ethylbenzene: $C_8H_{10} + 10.5\ O_2 \Rightarrow 8\ CO_2 + 5\ H_2O$

Xylene: $C_8H_{10} + 10.5\ O_2 \Rightarrow 8\ CO_2 + 5\ H_2O$

The range of dissolved oxygen in ground water is limited by the solubility of oxygen. At 25°C, the maximum solubility of oxygen, according to Henry's Law, is 8.32 mg/L (Manahan, 1991:94). In ground water systems, the actual concentration is usually 1/2 of the Henry's Law solubility at a given temperature (Wilson, 1994). Worth noting is that with a lower water temperature, which is likely with ground water, the water solubility of gases, like oxygen, actually increases (Manahan, 1991:94).

Nitrate. The use of nitrate as an anaerobic electron acceptor is wildly observed in intrinsic bioremediation. The primary reason is that nitrate is usually available in the ground water and provides a significant amount of redox energy to the microbes. The products of this biodegradation are carbon dioxide, water and molecular nitrogen, thus the process is said to be under denitrifying conditions. The likely BTEX biodegradation reactions are shown below:

Benzene: $C_6H_6 + 5\ NO_3 \Rightarrow 6\ CO_2 + 3\ H_2O + 5/2\ N_2$

Toluene: $C_7H_8 + 6\ NO_3 \Rightarrow 7\ CO_2 + 4\ H_2O + 3\ N_2$

Ethylb: $C_8H_{10} + 7\ NO_3 \Rightarrow 8\ CO_2 + 5\ H_2O + 7/2\ N_2$

Xylene: $C_8H_{10} + 7\ NO_3 \Rightarrow 8\ CO_2 + 5\ H_2O + 7/2\ N_2$

The highest expected concentration of nitrate in ground water is around 40 ppm (Cheng, 1994). Values have been reported above that which are usually influenced by the introduction of nitrates into the soil by human action (e.g. fertilizers). With the National Drinking Water Standard for nitrate at 10 ppm, it is unlikely that future sites will have levels of nitrate in ground water that are above natural values (Reinhard, 1994:141).

Manganese(IV). The use of Mn (IV) as an electron acceptor is more unique than other anaerobic biodegradation reactions. Only the most recent literature gives evidence of this reaction and the common existence of microbes that can use Mn(IV) is uncertain. A study of a crude oil spill near Bemidji, Minnesota gives direct evidence that it is utilized in anaerobic biodegradation (Baedecker, 1993: 576,584). A measured increase in Mn(II) within the plume over the background levels demonstrates that a redox reaction using Mn (IV) is occurring. The proposed stoichiometries considering Mn(IV) as electron acceptor are:

Benzene: $C_6H_6 + 15\ MnO_2 =>$

$6\ CO_2 + 15\ Mn^{2+} + 15\ O^{2-} + 3\ H_2O$

Toluene: $C_7H_8 + 18\ MnO_2 =>$

$7\ CO_2 + 18\ Mn^{2+} + 18\ O^{2-} + 4\ H_2O$

Ethylb: $C_8H_{10} + 21\ MnO_2 =>$

$8\ CO_2 + 21\ Mn^{2+} + 21\ O^{2-} + 5\ H_2O$

Xylene: $C_8H_{10} + 21\ MnO_2 =>$

$8\ CO_2 + 21\ Mn^{2+} + 21\ O^{2-} + 5\ H_2O$

Manganese oxide is considered insoluble and should be found in the soil matrix as the contaminant comes in contact with soil particles. Evidence from field studies indicated manganese oxide concentrations at 10.4 mg/L, however, this was the only solid article that addressed manganese concentrations (Baedecker, 1993: 576).

Iron(III). Many studies, including the one referenced for manganese reduction, confirms that iron has been used by microorganisms to biodegrade hydrocarbons (Borden, 1994: 181) Observations in decreased ferric iron, Fe (III) and hydrocarbons with measured increases in ferrous iron, Fe(II) show this to be a significant biodegradation reaction and even more common than a reaction with manganese. A probable BTEX degradation stoichiometries are as shown:

Benzene: $C_6H_6 + 30\ Fe(OH)_3 =>$

$6\ CO_2 + 30\ Fe^{2+} + 60\ OH^- + 18\ H_2O$

Toluene: $C_7H_8 + 36\ Fe(OH)_3 =>$

$7\ CO_2 + 36\ Fe^{2+} + 72\ OH^- + 22\ H_2O$

Ethylb.: $C_8H_{10} + 42\ Fe(OH)_3 =>$

$8\ CO_2 + 42\ Fe^{2+} + 84\ OH^- + 26\ H_2O$

Xylene: $C_8H_{10} + 42\ Fe(OH)_3 =>$

$8\ CO_2 + 42\ Fe^{2+} + 84\ OH^- + 26\ H_2O$

Iron oxide (and any other Fe(III) species) is insoluble in water and must also be part of the soil matrix, on the exterior of particles, to be used by microbes in biodegradation. Field concentrations of ferric iron are not well published, but a field study indicated 32 ppm Fe(III) in aquifers and other sources cite values up to 100 mg/L (Baedecker and others, 1993: 576; Borden, 1994: 182).

Sulfate. Offering lower redox energy than any of the previous electron acceptors, an anaerobic biodegradation reaction using sulfate would initiate after the higher energy species are either depleted or native microbes cannot acclimate to them. Yet, evidence that sulfate has been used in biodegradation is more common than evidence of iron or manganese use as electron acceptors. The theoretical biodegradation reaction using sulfate is:

Benzene: $C_6H_6 + 4\ SO_4 + 2\ H_2O => 6\ HCO_3 + 4\ HS$

Toluene: $C_7H_8 + 4.5\ SO_4 + 3\ H_2O \Rightarrow$

$7\ HCO_3 + 2.25\ H_2S + 2.25\ HS + 0.25\ H$

Ethylb: $C_8H_{10} + 5\ SO_4 + 3\ H_2O \Rightarrow$

$8\ HCO_3 + 2.5\ H_2S + 2.5\ HS + 2.5\ H$

Xylene: $C_8H_{10} + 5\ SO_4 + 3\ H_2O \Rightarrow$

$8\ HCO_3 + 2.5\ H_2S + 2.5\ HS + 2.5\ H$

Sulfate will be used in biodegradation as a dissolved ion and will flow with the ground water, as will oxygen and nitrate. However, sulfate is less conservative than nitrate as a dissolved species and begins to sorb to soil particles as water pH drops below 5. Figure 5 details this behavior.

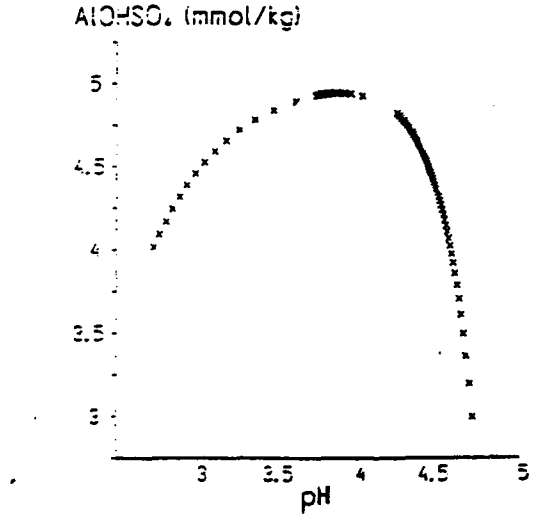

Figure 5. Sorption of SO4 as AlOHSO4 with changing pH. (Prenzel, 1994: 192).

Because ground water regularly remains between 6 and 8 on the pH scale, sulfate in not expected to sorb to the soil matrix in most aquifers. Expected concentrations of sulfate in ground water are approximately 50 ppm (Cheng, 1994).

Other Electron Acceptors. Carbon dioxide and even water can be used as electron acceptors by microorganisms (Borden, 1994: 182). These microorganisms are called methanogenic because they produce methane as a product of their degrading of hydrocarbons. These reactions offer less energy than sulfate reductions, but evidence of

their occurrence in the field is documented (Baedecker, 1993). Since these are the lowest energy reactions and this effort intends to portray a conservative representation of intrinsic bioremediation, these electron acceptors will not be considered in this work.

Mass Balance Relationship. The stoichiometry provides the basis of the mass balance relationships of electron acceptors to BTEX contaminant. The chemical reaction determines the mole ratio required for the contaminant and electron acceptor. The ratio of moles of contaminant per mole of electron acceptor was converted into mass of contaminant to mass of electron acceptor species. Table 3 displays the mass of contaminant (BTEX) that can degrade in the presence of one unit mass of electron acceptor (e.g. mass of benzene (mg) per mass of O2 (mg)).

Table 3. Mass Balance Factors

Compound:	O2	NO3	MnO2	Fe(OH)3	SO4
Benzene	0.325	0.252	0.060	0.024	0.203
Toluene	0.319	0.247	0.059	0.024	0.213
EthylB.	0.315	0.244	0.058	0.024	0.221
Xylenes	0.315	0.244	0.058	0.024	0.221

Summary

After analyzing hydrocarbon biodegradation and the application to JP-4 hydrocarbons, specifically BTEX, the literature indicates that intrinsic bioremediation is feasible. There are many parameters that influence the occurrence and rate of intrinsic bioremediation, yet the one that seems most critical is the existence of adequate electron acceptors. The quantity of electron acceptors in the aquifer appears to have the most influence on the rate of biodegradation and these quantities can be readily obtained from samples of the ground water and saturated soil. There remains some uncertainty in

intrinsic bioremediation which lies primarily in the existence of microbes in the native ground water that will acclimate to and consume all of the BTEX compounds. Yet, field studies give assurance that it is possible for all BTEX compounds to be depleted through intrinsic bioremediation using various electron acceptors.

III. Methodology

Overview

This methodology is separated into three distinct areas. The first area describes and analyzes the theoretical expectations that most affect intrinsic bioremediation. Discussed is the source of the pollution considered for this model (JP-4) and what unique considerations must be made in order to apply the concepts and expectations to this pollution source. A biodegradation model will be proposed with two distinct cases to which it will be applied. Lastly, the application of the findings will be made to a usable field tool in order to evaluate intrinsic bioremediation.

Basis of Intrinsic Bioremediation Analysis

Considerations. According to discussions of intrinsic bioremediation with Dr. John Wilson, USEPA R.S. Kerr Environmental Research Laboratory, the quantity of the electron acceptors is a key rate limiting factor in biodegradation (Wilson, 1994). Therefore, the hypothesis that this research proposes is that the availability of electron acceptors in a contaminated aquifer can be used as an accurate indicator of the theoretical duration of intrinsic bioremediation until the site reaches a clean level.

If the native microorganisms in an aquifer can aerobically or anaerobically degrade hydrocarbons and are able to use one or more electron acceptor, they will use those available electron acceptors until the petroleum or the acceptors are consumed. If all other site conditions favor hydrocarbon biodegradation, this work will assume that if there exists a quantity of electron acceptors over a finite aquifer volume that, according to the mass-balance of electron acceptor to BTEX, the BTEX concentration will be reduced to the availability of the electron acceptors.

Other means of predicting plume biodegradation were considered. Observations have been made in regard to the combined effects of contaminant transport and

simultaneous degradation. In field studies with continuous sources, contaminant plumes reach a steady state condition where the degradation rate at the edge of the plume is equal to the flow rate of the constituent at a given distance from the source. Therefore, a plume will reach a maximum extent of travel within the aquifer. However, predicting the extent of the plume with this result is uncertain and very dependent on many random factors. One of these uncertainties would be reaeration rate to anoxic or oxygen-depleted water down gradient.

Proposition. As discussed, the quantity of electron acceptors at a site can directly influence the success of intrinsic bioremediation at that site. This research will focus on this conclusion to develop a prediction of intrinsic bioremediation duration given initial quantities of electron acceptors and contaminant. The electron acceptors will include: O_2, NO_3, Mn(IV), Fe(III) and SO_4 as all have a theoretical basis and as well as observed results for use in biodegradation.

The basis of this methodology is completing a mass balance of BTEX to electron acceptor according to the stoichiometric relationship of degradation. A relationship will be established between the quantity of electron acceptors used to degrade the BTEX constituents compared to the other significant constituents of JP-4. The degradation scenarios can be simplified to focus on BTEX degradation only while taking into consideration the effect other compounds will have on the supply of electron acceptors.

Analysis of Pollution Source

In our consideration of only modeling the BTEX biodegradation, the affect of other hydrocarbons present must be considered. The selected pollution source is JP-4 and it is a mixture of numerous hydrocarbons to include aliphatics, alicyclics and aromatics.

Organic Compounds. Aliphatic compounds are straight or branched chain organic compounds. They may be alkanes, or saturated compounds, and contain only single

covalent bonds. Also included may be unsaturated compounds that contain double bonds, such as alkenes or even triple bonded compounds. An example of an aliphatic is hexane which is an alkane.

Alicyclic hydrocarbons will contain single bonds, but the chains will form a circle with branches of hydrogen atoms or more carbons attached. One alicyclic is ethylcyclopentane.

Aromatic compounds all contain a benzene ring or a combination of rings. The benzene ring is defined as six carbon atoms with three bonds using a single electron pair and the other three bonds using two electron pairs at any given time. Aromatics include benzene and alkylbenzenes which have one ring and are usually the most water soluble constituents of a hydrocarbon mixture. The alkylbenzenes are considered to have a toxicity which, coupled with their high solubility, make this class of compounds of highest environmental concern. Other aromatics include naphthalene, two rings and no branches, and polyaromatic hydrocarbons (PAHs) that have three rings or more.

JP-4 Composition. The typical hydrocarbon composition of JP-4 is listed in appendix I, Table A1-1, along with the respective mass fraction and solubility. Some solubility figures are not published, but in that case relative solubilities were used. The rule followed was that solubilities of branched hydrocarbons is usually as much or less than the solubility of the respective base hydrocarbon (Schwarzenbach, 1993: 107). By multiplying the mass fraction by the solubility of each constituent, we obtain a relative, dissolved constituent, mass factor of the JP-4 constituents when the fuel contacts ground water (Lyman and others, 1992: 230). This relative mass factor is used as a scale in comparing the mass in solution of the dissolved constituents with the higher factors indicating a higher relative mass in the hydrocarbon plume.

Potential to Biodegrade. In regard to their suitability for aerobic or anaerobic biodegradation, the single-ring aromatics appear to be attractive to microorganisms and

very likely to biodegrade. Evidence of alkylbenzene biodegradation has already been referenced. There is little published on the half-lives of aliphatic compounds, but the aerobic and anaerobic biodegradability of the straight-chained saturated aliphatics is generally accepted. Unsaturated and branched aliphatics have a less certain biodegradability (Chapelle, 1993: 329). Alicyclics are much less prone to biodegradation and if they do, respective half-lives are much greater than with aromatics (Chapelle, 1993: 334; Howard and others, 1991).

Multi-ring aromatics appear somewhat different. Two-ring compounds like naphthalene degrade readily, though a bit slower than most alkylbenzenes. PAHs are not likely to degrade at all in comparison to the other hydrocarbons (MacKay and others, 1993; Howard and others, 1991).

A key estimate needed is what fraction of the electron acceptors will be used to biodegrade the BTEX compounds compared to other hydrocarbons found in JP-4. This fraction was approximated from the relative mass factors of BTEX compared to the relative mass factors of all biodegradable hydrocarbons in JP-4. The calculation of this value were accomplished in appendix I, Table A1-2. The relative mass factors of all biodegradable hydrocarbons were added to indicate a total degradable mass in solution. The relative mass factors of the BTEX compounds were divided by the total degradable mass in solution. This fraction was corrected for any unaccounted JP-4 hydrocarbons. The degradable mass in the plume composed of BTEX was computed to be 81%. Therefore, 81% of the initial mass of electron acceptors will be assumed to be used for BTEX biodegradation.

Also assumed in this research is that the relative mass composition of total BTEX was constant after the JP-4 contacts the water. The fraction of an individual compound contribution to total BTEX was calculated from the relative mass factors of the individual BTEX compounds to the total BTEX mass factor. The results are in Table 4.

Table 4. Mass Composition of Dissolved BTEX

Contaminant	Benzene	Toluene	Ethylbenzene	Xylenes
% of BTEX	41	40	6	13

Modeling Procedures for Intrinsic Bioremediation

The goal of this research is to develop a simple prediction of intrinsic bioremediation duration based on the availability of electron acceptors. A key objective is to allow to model to be simple enough that it can be constructed in a concise time period and yet represent actual intrinsic bioremediation of BTEX. This simple model will indicate a theoretical expectation of intrinsic bioremediation performance.

Several contaminant fate and transport models have been devised to quantify how the various contaminant properties and hydrogeologic parameters affect the contaminant concentrations. One model in particular is well referenced in the literature which is named BIOPLUME II™. This model was developed by Rice University and was used in a thesis effort by Capt W. Potts (GEE-93S) to analyze intrinsic remediation. BIOPLUME II™ is a numerical model in FORTRAN code than used the finite-difference approximation of ground water flow (Rafai and Bedient, 1993: 7-1). The author of the transport model and Capt Potts both completed sensitivity analyses on the model and arrived at similar results. It was found that the parameters which most affect the final concentration of a contaminant, using this model, include hydraulic conductivity, the reaeration coefficient, and the anaerobic decay rate (Potts, 1993). However, the individual anaerobic decay processes couldn't be simulated with individual electron acceptor concentrations as an input.

To address the specific anaerobic processes and the respective electron acceptor quantities, it was decided to develop an original simulation model. This model will be

developed to meet this objective conceptually and then the mathematical representations constructed accordingly.

Conceptual Model. A number of simplifying assumptions will be made to develop this intrinsic bioremediation model. The first assumption is that the most likely threat of BTEX exposure lies in the most direct path of ground water flow so the high concentration along the center line of the plume will characterize the width of the plume. The next significant assumption is that the plume will not disperse either in the longitudinal or traverse directions. Therefore all biodegradation will occur within an unchanging boundary. The moving plume will be considered to be influenced by advection only. The pollution source for this model is not continuous. To achieve constant advection, this research will assume the contamination occurs in a homogenous, isotropic and unconfined aquifer with a constant hydraulic gradient.

Reaeration rates are uncertain and suggested to be of little affect to contaminants well below the surface of the water table so they will be considered negligible. The biodegradation will occur according to the redox potential of the five electron acceptors with the highest redox energy: O2, NO3, Mn(IV), Fe(III), and SO4. All first-order degradation rates for aerobic or anaerobic biodegradation will be constant for the respective process. The microbes are assumed to be acclimated to BTEX so there will be no lag time computed in this biodegradation model.

The retardation of the plume is influenced by the soil organic content. Representative values for organic content will be considered and a retardation computed. Even though each of the BTEX compounds will not retard equally because each has a different organic carbon partition coefficient, this model will assume that the BTEX will retard according to the constituent that is retarded the least.

To analyze this type of intrinsic bioremediation model, this methodology will separate a JP-4/BTEX degradation event into two distinct observations. First this

research will consider that the plume of dissolved pollutants is static and occupies only the space within the immediate site. The microorganisms in the plume will only have the initial electron acceptors within the plume to accomplish intrinsic bioremediation. The second examination will be of a dynamic system of contaminant flow and concurrent degradation. The advective flow of ground water and plume motion will introduce new electron acceptors for use by the microbes.

Static Plume Model. The primary assumption for this model is that the plume is static in the aquifer which is the most conservative with respect to intrinsic bioremediation success. The only electron acceptors (EA) available for biodegradation are those within the bounds of the plume itself and this research considers electron acceptor availability as the process limiting factor. Analyzing this model will encompass computing the available electron acceptors for degradation and computing the change in BTEX according to the mass balance factors of the electron acceptors to BTEX based in the stoichiometric relationships.

The equation to calculate the concentration of contaminant after biodegradation is:

$$P(EA)=P.o-MB*EA.avail$$

where: P(EA) = Concentration of pollutant (one of BTEX) after degrading with a given electron acceptor [ppm or m/l^3]

P.o = Initial concentration of pollutant [ppm or m/l^3]

MB = Mass balance factor (see Table 3)

EA.avail = Expected electron acceptors available to pollutant P [ppm]

Note: The units expressed for all variables are in generic mass, time, and length units.

The calculation of EA.avail is for a specific pollutant and will be computed from three factors. First is the initial quantity of the respective electron acceptor. Second is ratio of the specific pollutant to the total BTEX. Third is an adjustment factor for the

different decay constants which will be called an electron acceptor balance factor (EA.bal). A faster decay constant for a given pollutant (e.g. toluene) means more electron acceptors will be used in a given time for its degradation than a pollutant with slower decay constant (e.g. benzene). The EA balance factor will then modify the calculation of EA.avail according to this difference in decay constants. This balance factor is c ed from the ratio of the natural log of the decay constant for a pollutant divided by the average of the natural logs of the decay constants for all BTEX compounds. The equations for EA.avail and EA.bal are:

$$EA.avail = EA.o * (\frac{P_i}{\sum P_i}) * EA.bal$$

where: P.i = pollutant of interest (one of BTEX) [ppm]

SUM (P.i) = Total BTEX [ppm]

and:

$$EA.bal = (\frac{\ln(k_i)}{avg(\ln(ki))})^{-1}$$

where: k.i = the exponential decay constant for P.i [t^{-1}]

The EA balance factor equation is designed so the factors will average to one. This will mean that no net gain or loss of the electron acceptors is experienced. Tables 5 and 6 show the EA.bal factors for the aerobic and anaerobic decay constants to be used in this research to demonstrate that the average is unity.

Table 5. Aerobic EA balance factors

	Benzene	Toluene	Ethylb.	Xylene	Average
Decay Constant (k.i)	1.0 E-3	1.7 E-3	5.0 E-4	1.4 E-3	1.14 E-3
EA.bal	0.999	1.072	0.903	1.043	1.004

Table 6. Anaerobic EA balance factors

	Benzene	Toluene	Ethylb.	Xylene	Average
Decay Constant (k.i)	6.9 E-5	2.2 E-4	1.4 E-4	1.5 E-4	1.4 E-4
EA.bal	0.931	1.057	1.007	1.012	1.002

If the results of the static plume analysis show that the quantity of electron acceptors is ample for complete biodegradation to the cleanup level, then we can conclude that intrinsic bioremediation will not be limited by the quantity of electron acceptors. Assuming that other factors are optimum for biodegradation, the degradation will continue until the contaminant is depleted. However, this conclusion has not considered biodegradation kinetics. Decay rates and ground water flow conditions can then be generally applied to determine the time expected to degrade the contaminant. The time to biodegrade the BTEX to the new concentration, P(EA), can be found from the exponential decay equation:

$$P(EA)=Po*\exp(-k*t)$$

And the time of degradation for P is:

$$t = \ln(\frac{P(EA)}{Po}) * \frac{1}{-k}$$

where P(EA) = New concentration of pollutant [ppm]

Po = Initial concentration [ppm]

k = Exponential decay constant [t^{-1}]

The approximate plume migration is calculated using this estimated time value and other site conditions. This migration is assumed to occur without the introduction of

new electron acceptors into the plume. These site parameters include hydraulic gradient, hydraulic conductivity, porosity and organic fraction in the aquifer soil. These values are combined to define two different features of contaminant transport: linear velocity of the ground water and plume retardation factor. The equation for plume migration velocity is:

$$V_{contam} = \frac{V_{gw}}{R}$$

were: V.gw = Linear velocity of the ground water [l/t]

R = Retardation factor of the plume

The linear velocity of the ground water is defined as:

$$V_{gw} = K^{*}(dh/dL)^{*}\frac{1}{\eta}$$

where: K = Hydraulic conductivity [l/t]

dh/dL = hydraulic gradient

η = porosity

and the retardation factor is defined as:

$$R = 1+((1-\eta)/\eta)^{*}\rho^{*}K_{oc}{}^{*}f_{oc}$$

where: ρ = density of solids = 2.65 [m/l^3]

K.oc = partition coefficient: organic carbon to water

f.oc = organic carbon fraction of the aquifer soil

These factors and equations will be compiled onto a Quattro Pro v5.0 worksheet to model various initial values and determine time and distance quantities for these values.

Dynamic Plume Model. If this evaluation doesn't show there are adequate electron acceptors to degrade a static plume, we need to consider the introduction of electron acceptors into the plume. The factors which affect this condition the most are ground water velocity, contaminant retardation and biodegradation rates with the latter being the element with the most uncertainty. The dynamic plume case requires that the concentrations of contaminant be calculated similar to the static plume, but according to time steps and limited by the electron acceptor mass.

The ground water flow through the retarded plume will introduce water soluble electron acceptors from the rear of the plume. Those electron acceptors that are insoluble will be introduced into the plume from the front as it migrates through the saturated soil. This model will simulate water flow through equal portions of this plume over discrete steps of time while considering the biodegradation kinetics and electron acceptor availability. All other factors that affect biodegradation (e.g. microbe acclimation) will be considered at their optimum.

The length of the plume will be segmented according to a given section length in order to obtain accurate biodegradation in different locations within the plume. Figure 6 shows the movement of ground water and the plume according to the descriptions above over three time steps. The figure is drawn as if the observer moves with the plume, so the ground water will move from the rear of the plume forward and the soil will appear to move from the plume front to the rear.

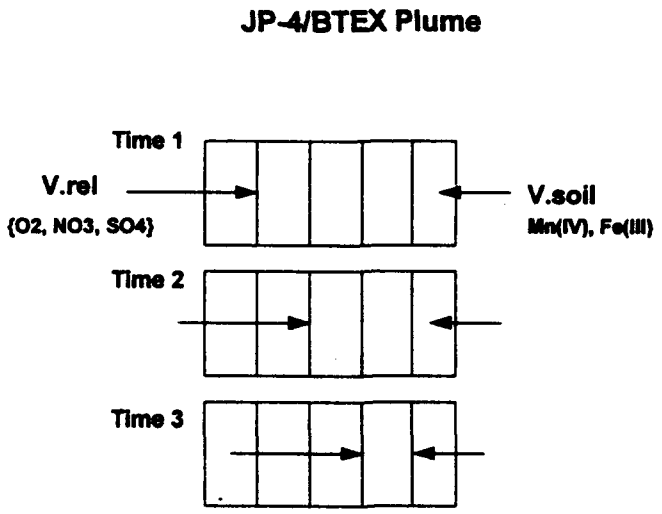

Figure 6. Diagram of electron acceptor movement into plume via ground water or soil.

This model will initially use 10 plume sections to segment the plume length. Again, the degradation in this dynamic model will limit biodegradation by electron acceptor quantity or the time available to degrade. Computing pollutant concentrations after decay will occur according to these two factors and in the order of electron acceptor use. The order which the electron acceptors are used will match the redox scale shown in Figure 3. The individual calculation of pollutant concentration will follow the qualitative flowchart shown in Figure 7.

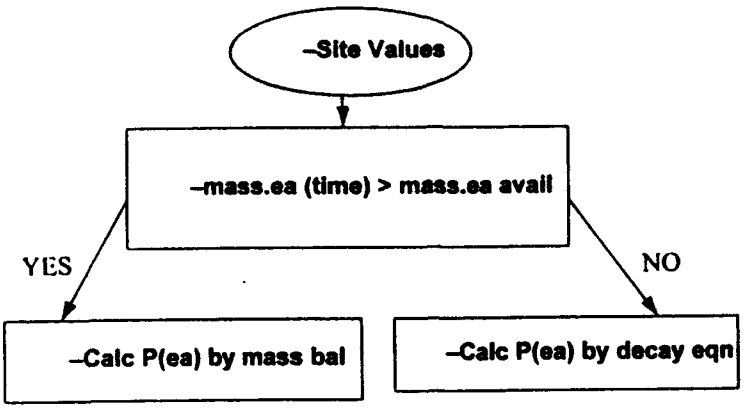

Figure 7. Qualitative computation of pollutant concentrations in dynamic flow model.

The equation for the mass of EAs needed in the time available for biodegradation (t.avail) is:

$$mass.EA=[Po-Po*\exp(-k*t.avail)]*\frac{1}{MB_i}$$

The mass of EAs available is computed in the same manner used in the static model. If the mass of electron acceptors is limiting in the biodegradation calculation, then the concentration of contaminant P(EA) is calculated according to the P(EA) equation used in the static model. If time is the limiting factor, the concentration of contaminant is calculated using the decay equation:

$$P(EA)=Po*\exp(-k_i*t.avail)$$

The variable "t.avail," as the time available for biodegradation, is usually the time step value. If biodegradation using a given electron acceptor depletes this electron acceptor within a time step, the next electron acceptor is used and t.avail must be corrected for the time already spent using the previous EA. This time spent using the previous EA could be either aerobic or anaerobic biodegradation so the equation must be able to compute each case. For example, in the time step where the oxygen is depleted and anaerobic

decay with nitrate begins, t.avail is equal to the time step reduced by the time spent on aerobic decay. The equation for t.avail is shown below.

$$t.avail = ts - [(\ln(P(O2)/Po) * \frac{1}{k1} + (\ln(P(EA_i)/P(O2)) * \frac{1}{-k2}]$$

where: ts = Time step [days]

k1 = Aerobic decay constant [$days^{-1}$]

k2 = Anaerobic decay constant [$days^{-1}$]

One correction factor is applied to the calculation of electron acceptors available which is different from that of the static case. The ratio of relative ground water velocity times the time step to the section length determines the fraction of electron acceptors moving from one section of the plume to another. This relationship is described as:

$$EA_{secx} = Vrel * \frac{ts}{x} * EA_{secx_{-1}} + (1 - Vrel * \frac{ts}{x}) * EA_{secx}$$

where: EA_{secx} = Electron acceptor quantity in section x

EA_{secx-1} = Electron acceptor quantity in section previous to section x (with respect to ground water motion)

Vrel = Relative velocity of ground water into plume

x = section length within plume

The factors above compile the equations needed to model the dynamic plume simulation of intrinsic bioremediation. Because of the elementary relationships in these equations, the Quattro Pro spreadsheet software is also suited for this simulation of the dynamic model. An advantage of the software is that it gives a full display of contaminant values throughout the plume at every time interval. This display makes the values readily available to note trends in the data. Also, extracting these values from the worksheets is an automated function within the software.

Aerobic Front Analysis. This is an addition to the methodology after the sensitivity analysis was completed. As the conclusions will further discuss, the use of the availability of the anaerobic electron acceptors is not a primary factor in predicting the time at which the plume reaches "safe" concentrations. However, the boundary between the aerobic portion of the plume and the anaerobic portion may be well defined, described here as the aerobic front. Using simulations from the dynamic degradation model, the aerobic front will be analyzed for a range of parameters to see if the movement of the front through the plume is at a constant rate. This movement will be characterized by defining the position of the front in relation to a clean level of the contaminants. Since we are using 10 ppm Total BTEX as the standard for this model, the respective fraction of 41% benzene per total BTEX (or 4 ppm benzene) will be used as this acceptable level. Because benzene degrades slower than other BTEX compounds, 4 ppm benzene is a conservative estimate of this 10 ppm BTEX cleanup level. The position of the aerobic front verses time will be plotted to determine the trend of the front velocity. The aerobic front velocity will be referenced as "AFV10" because it is defined at 10 ppm total BTEX.

Aerobic Front Velocity Predictor. The three parameters of interest here are the initial BTEX loading (BTEX), initial oxygen loading (O2) and relative velocity of the ground water entering the plume (Vrel). If the speed of the aerobic front is constant given constant parameters, then it will be determined if the magnitude of the front velocity can be statistically modeled as a function of these parameters. This general linear model will be constructed through a linear regression of the three parameters and any higher order terms derived from them. A generic general linear model is illustrated by the following equation:

$$Y=\beta+\beta*X1+\beta*X2+\beta*X3+\ldots+\varepsilon$$

Where each X_i is a predictor variable for the dependent variable Y. (Neter and others, 1989: 229; Devore, 1991: 526).

The end result of this analysis of the aerobic front simulation will be this relationship between BTEX, O2, Vrel and a predicted velocity of the aerobic front (AFV10). By comparing this velocity to the approximate plume length, the time can be found for the aerobic front to travel this distance. Once the front reaches the leading edge of the plume, we can expect that the plume is fully degraded to the 10 ppm BTEX level. This tool of predicting degradation time is intended to provide the site manager with information that he or she could use in selecting intrinsic bioremediation as a method to study for possible employment.

Judging the success of intrinsic bioremediation will be a qualitative assessment of the potential risk of the plume contaminants coming in contact with a neighboring population as well as other factors specific to the contamination site. Using this prediction for intrinsic bioremediation duration as a possible value and computing a corresponding distance traveled, the site manager can determine if this can meet local requirements. Assuming that the time required and distance of plume travel are acceptable, intrinsic bioremediation should be investigated as the restoration method for this site. The subsequent course of action for a site manager would be to implement a full-scale site characterization to demonstrate intrinsic bioremediation occurrence and effectiveness.

Application to Field Data

The primary thrust of this research is to provide an elementary relationship between site parameters and intrinsic bioremediation success. The parameters used as predictors in the general linear model described above can be directly found or estimated from site measurements. The initial characterization of the site should include

measurements for BTEX compounds, the background electron acceptor concentrations with water temperature, hydraulic gradient, hydraulic conductivity, porosity, and natural organic content of aquifer. From this data, BTEX, O2, and Vrel can be determined and the aerobic front velocity computed for this site.

Areas of Uncertainty

There are several parts of the biodegradation process that will be specific to each site and difficult to predict. The variability will either be accounted for or a simplifying assumption made to select a reasonable value. Such random factors include the availability of microbes that are able to biodegrade aromatic hydrocarbons, aerobic and anaerobic degradation rates and the lag times associated with microorganisms being acclimated to its newly contaminated environment. Another random factor is the actual quantity of BTEX that will accumulate in the ground water following the release of a known quantity of JP-4. Predicting the expected BTEX concentrations from a specific amount of JP-4 is imprecise as numerous uncertainties are involved. The reverse is also true as BTEX concentrations cannot give the precise quantity of JP-4 released. Therefore, this model will use BTEX concentrations as found in ground water as its input.

List of Assumptions. To examine the uncertainty that exists in this prediction of intrinsic bioremediation, the following is a compilation of the assumptions made in this methodology. Also included is an assessment of whether the assumption will encourage the model to be conservative or non-conservative with respect to the time for biodegradation to take place. If the assumption can be either conservative or non-conservative to the results of the model, this will be noted. The definition of a conservative assumption is one that encourages more time for biodegradation than would be realistic.

The legend for this list is: C = conservative, NC = non-conservative, C/NC = Neither conservative nor non-conservative.

Assumptions	Effect
A. Site conditions	
1. Homogeneous, isotropic, unconfined aquifer	C/NC
2. Darcy's Law is valid for this site	C/NC
3. Microbes in the area will degrade petroleum	NC
4. Concentration of BTEX is constant	C/NC
5. Concentration of electron acceptors is constant	C/NC
B. Process/Model	
1. Availability of electron acceptors is the process limiting factor	C/NC
2. Plume will not disperse	C
3. Degradation will occur according to 1st order decay relationship	C/NC
4. Decay constants will not change for respective degradation process	C/NC
5. Decay constants are mid-range literature values	C/NC
5. BTEX retardation will be constant for all compounds	C
6. Electron acceptors will be allocated to BTEX from other hydrocarbons by ratio of expected mass in solution	C/NC
7. Electron acceptors will be at background levels within plume at the start of simulation	C/NC
8. Lag times for microbe acclimation will be zero	NC

9. Electron acceptor input values will be reduced
to 81% of initial site value C

10. Plume Concentration is taken as highest value
and uniform for the length of the plume C

11. Aquifer reaeration is negligible C

The overall assessment of the simulation model is that it will produce conservative results of intrinsic bioremediation. The primary driver of this appraisal is the assumption that the plume will not disperse. Dispersion will increase the volume of the plume and thereby allowing more microbes and electron acceptors to act on the available BTEX. For example, given a plume traveling from day 50 to day 200 in an aquifer with a longitudinal dispersivity of 6 feet, transverse dispersivity of 0.6 feet and a water velocity of 0.5 ft/d, the plume volume could increase by 300% and the cross sectional area may increase by 100% (Domenico and Schwartz, 1990: 365-374). Dispersivity and velocity values can change by magnitudes, yet this example computation indicates that dispersion can significantly affect plume concentrations.

The other assumptions listed as conservative have more uncertainty than the dispersion, yet all lend themselves to produce conservative simulation results compared to actual intrinsic bioremediation. The two non-conservative assumptions are also seem limited as to the degree they may or may not be non-conservative. As a whole, these assumptions should produce conservative results on average though the range of uncertainty may push the results to be slightly non-conservative to distinctly conservative. Considering the no-dispersion assumption along with these other assumptions, the simulation model is expected to remain conservative for recreating a typical intrinsic bioremediation scenario.

IV. Remediation Model and Data Analysis

Static Plume Analysis

Our first consideration for intrinsic bioremediation is the static plume. The question under investigation is if there are adequate quantities of electron acceptors available in the ground water to facilitate complete biodegradation of BTEX compounds.

Mass Balance Analysis. Table 3 provides us the mass balance ratio of pollutant to electron acceptor for biodegradation reactions. Using this information, a simple comparison of pollutant and electron acceptor concentrations can be made for a given site. A JP-4 plume, with possible BTEX concentrations, is considered. The initial concentrations are given for each contaminant and electron acceptor. The values given Table 7 are the concentration of the respective contaminant after being degraded with the specific electron acceptor.

Table 7. Static Plume Mass Balance Calculation

	JP-4 INTRINSIC BIOREMEDIATION: STATIC CASE					
	Initial values	O2	NO3	MnO 2	FeOH 3	SO4
Contaminant	in ppm	4	20	5	30	25
Benzene	8.2	7.8	6.2	6.1	5.9	4.3
Toluene	8	7.6	5.9	5.8	5.5	3.7
E.benzene	1.2	1.1	0.9	0.9	0.9	0.6
Xylenes'	2.6	2.5	1.9	1.9	1.8	1.2
Total BTEX=	20	18.93	14.92	14.68	14.10	9.85

Given a clean up standard of 10 ppm and this loading of 20 ppm total BTEX with corresponding electron acceptors, the microorganisms at this site could biodegrade the BTEX to a total concentration of 9.85 ppm. Because this value is less than 10 ppm total BTEX, we conclude that the microbes at this site have adequate reactors to biodegrade the BTEX to an acceptable level without introduction of additional electron acceptors. With the other conditions suitable for intrinsic bioremediation, we can expect that the microbes will degrade the petroleum to this level given adequate time.

Kinetics Considered. This conclusion itself may not satisfy a site manager as a prediction of intrinsic bioremediation feasibility. Consideration of the time expected for this biodegradation to occur and the distance the plume may travel will presumably be of interest to the manager. The time to degrade can be predicted from possible first-order degradation constants (k) for the BTEX compounds. Middle range aerobic and anerobic biodegradation constants from the literature are shown in Table 8.

Table 8. Mid-Range Exponential Decay Constants

Decay Constants:	Aerobic (hrs^{-1})	Anaerobic (hrs^{-1})
Benzene	.00103	7E-5
Toluene	.00165	2.2E-4
Ethylbenzene	.00048	1.4E-4
Xylenes	.00138	1.5E-4

Using these equations and obtaining time and migration values, a site manager can obtain a prediction of plume biodegradation. The manager can use this information in their decision making process about remediation avenues.

If the concentrations of BTEX and electron acceptors are such that the mass balance within the plume is unfavorable to complete depletion of the contaminant, we then consider electron acceptors entering the plume. This situation is investigated with the dynamic plume model.

Dynamic Plume Analysis

Before simulations of intrinsic bioremediation were run with the dynamic plume model, the author first completed the check of the consistency of calculations of the model as affected by the selection of time step and section length. The second action completed was a sensitivity analysis to see which parameters affected the model and the extent of that affect. Third, the limitations of the model will be discussed and the limitations observed in the software used for the model. Lastly, the analysis of the aerobic front will be presented. Included will be a validation of the constant velocity of the aerobic front and which parameters affect this front velocity.

Ensuring Model Consistency. The dynamic degradation model is set up to simulate biodegradation over time within a given amount of space. How the plume space

and degradation time are discretized may affect the consistency and viability of the model. The time step was initially set at 0.05 day and the section length at 0.2 ft. The concentration of benzene was calculated over time and at a given distance into the plume. Below are results of this calculation for time steps: 0.05, 0.1, 0.2, 0.3.

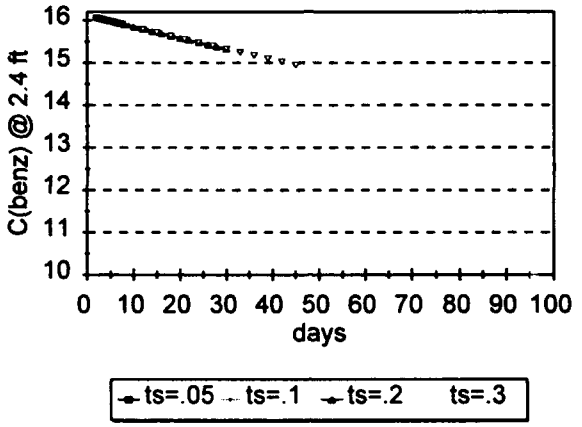

Figure 8. Time Step Analysis: ts=0.05 to 0.3 day at x = 2.4 ft
where:ts = time step; x = position in plume.

All four time step values result in consistent simulation results as the degradation lines overlap each other. For time steps to 0.3 day, the data indicates that the time step change doesn't alter the calculated concentrations of the contaminants to a significant degree. This analy: was repeated with progressively larger time increments and at respectively larger section lengths of 0.4 ft, 0.6 ft, 1.2 ft and 2.4 ft so that the data represents the biodegradation of benzene at the same location in the plume (2.4 ft from the rear). Figures 9 through 12 show the simulation results with variable time steps.

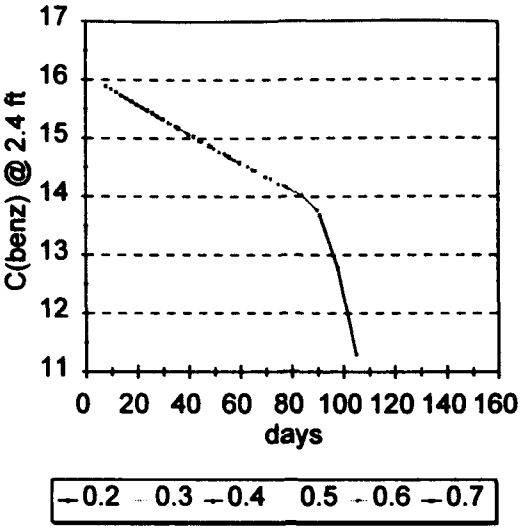

Figure 9. Time Step Analysis: ts = 0.2 to 0.7 day at x = 2.4 ft

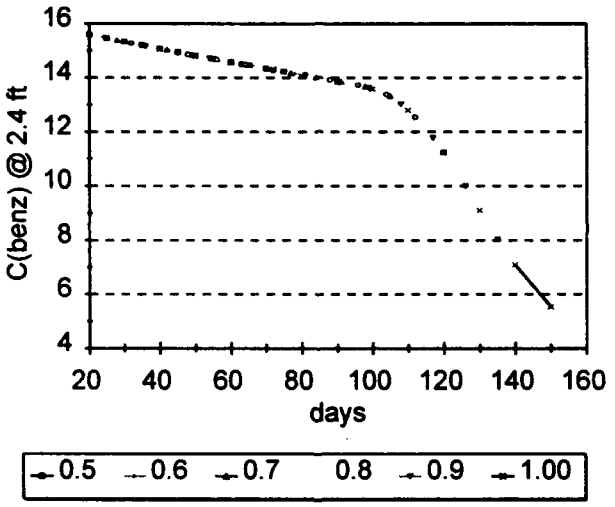

Figure 10. Time Step Analysis: ts = 0.5 to 1.0 day at x = 2.4 ft

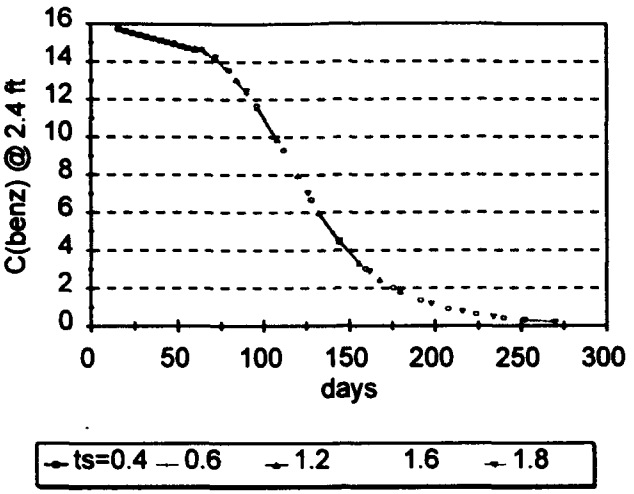

Figure 11. Time Step Analysis: ts = 0.4 to 1.8 days at x = 2.4 ft

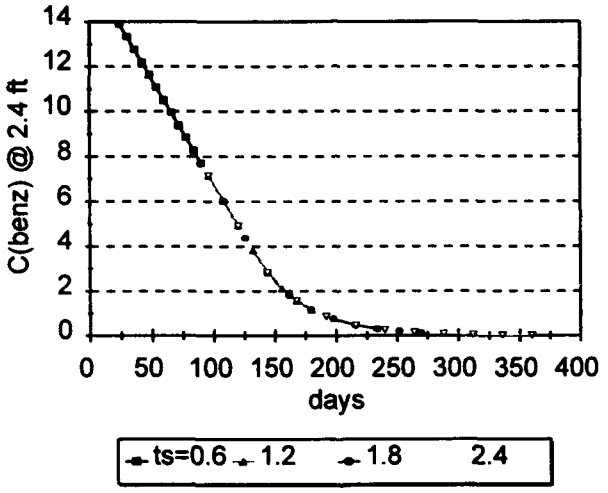

Figure 12. Time Step Analysis: ts = 0.6 to 2.4 days at x=2.4 ft

Each plot of the benzene concentrations over time using various time steps shows no detectable variations with a given section length. This shows that changing the simulation time step up to 2.4 days has no significant affect on the accuracy of the model. The next examination will be on the affect that the section length has on model consistency. Because the represented data is of the same location and with different section lengths, we can compare values from each plot at the 40 and 100 day point and

observe if the change in section length introduces an error in the computations of the model. The comparison is shown in Table 9.

Table 9. Comparison of Benzene Values at 2.4 ft.

Section Length: (ft)	0.2	0.4	0.6	0.8	1.2	2.4
C(Bz) at 40 Days	15	15	15	15	15	12
C(Bz) at 100 Days	-	13	13	13	12	6

The comparison of calculated benzene values at various section lengths indicates a discrepancy beginning at a section length of 1.2 ft and more noticeable at a section length of 2.4 ft. The analysis of section length was extended to determine a more specific value where the section length induces inconsistency into the model. The analysis began with computations of benzene concentrations over time using a constant time step of 0.5 day. The range of section length values were 0.26 ft to 1.5 ft. The data was initially compiled at common points in the plume of 2.8, 4.0, and 6.0 ft from the rear of the plume. These data plots are shown in Figures 13, 14 and 15.

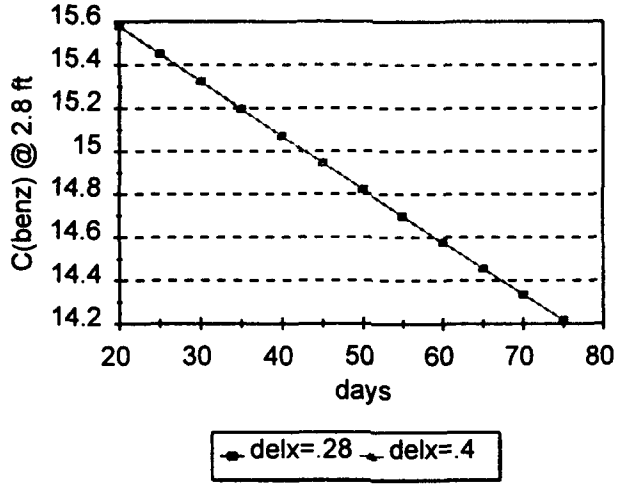

Figure 13. Section Length Analysis: section length=0.28, 0.4 ft at x= 2.8 ft

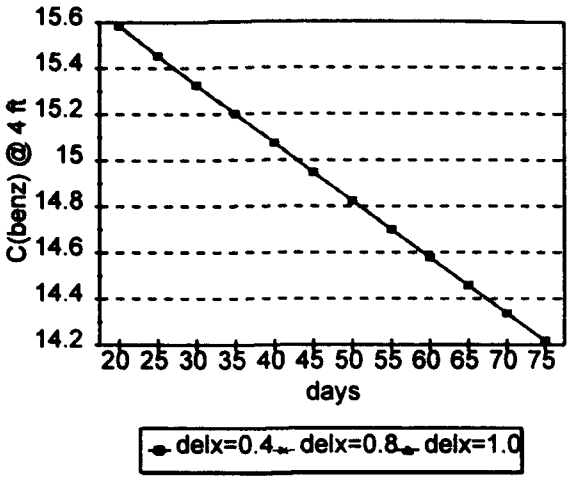

Figure 14. Section Length Analysis: section length = 0.4, 0.8, 1.0 ft at x = 4 ft.

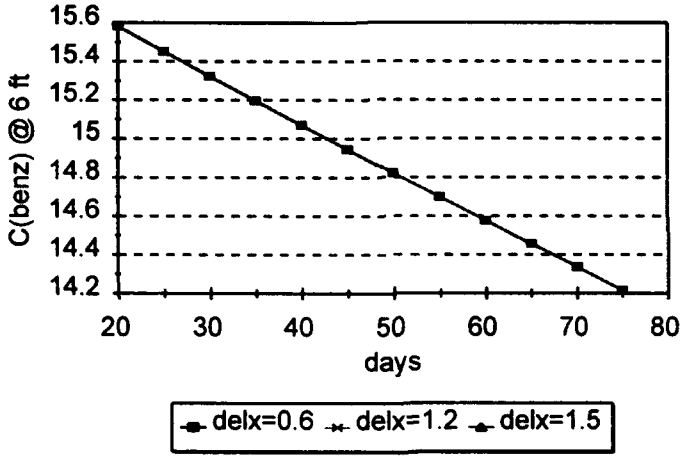

Figure 15. Section Length Analysis: section length = 0.6, 1.2, 1.5 ft at x = 6 ft

The three figures all show equivalent degradation values for their given section lengths. Two additional plume locations closer to the front of the plume were analyzed in the same manner. The positions selected were 2.4 ft and 3 ft. The data is shown in figures 16 and 17.

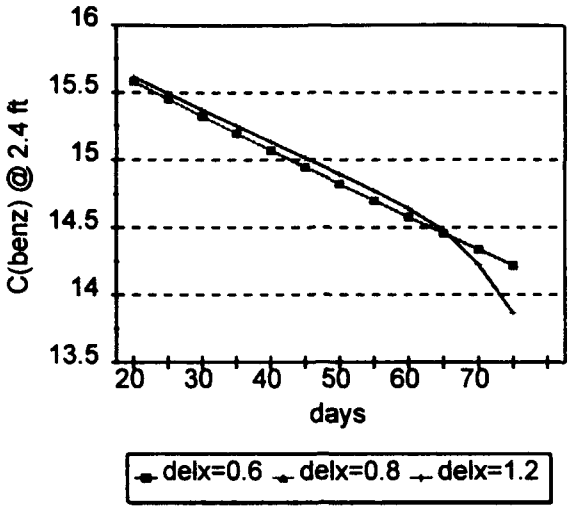

Figure 16. Section Length Analysis: section length =0.6, 0.8, 1.2 ft at x= 2.4 ft

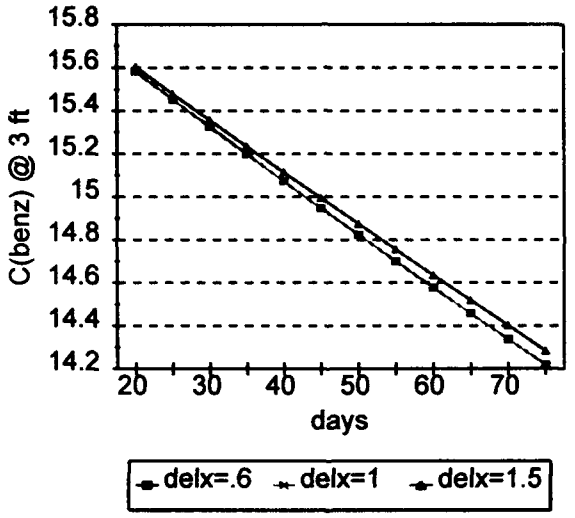

Figure 17. Section Length Analysis: section length =0.6, 1.0, 1.5 ft at x = 3 ft.

The data shows that the series with section lengths of 1.2 and 1.5 ft deviate from the other data at their respective positions. The section lengths of 1.0 ft and less demonstrate no deviations in the calculations of the benzene values.

The preceding analysis demonstrated that the section length did appear to affect the accuracy of computations by the dynamic biodegradation model. Values above 1.0 foot produced uncertain results within the plume, especially at locations near the rear of the plume. Time step changes, given a constant section length, did not deviate in the

range of values tested. For the remainder of the simulations, this analysis will use a constant time step of 0.5 and section lengths of 1.0 ft or less.

Sensitivity Analysis. The parameters that the literature indicated should have the most affect on the dynamic model of biodegradation were applied to the model to determine the influence they had on the outcome of the dynamic model. The range of values and a likely mid-range are shown for each parameter in Table 10 below.

Table 10. Parameter Range Values

Parameter: Quantities-ppm	Mid-Range Value	Low Value	High Value
Benzene	14	0	1000
Toluene	13	0	500
Ethylbenzene	2	0	100
Xylenes'	4	0	100
O2	4	0	5
NO3	20	0	40
MnO2	5	0	10
Fe(OH)3	50	0	100
SO4	25	0	50
Parameter: Aquifer	Mid-Range Value	Low Value	High Value
Hydraulic Conductivity-ft/d	50	.01	500
Hydraulic Gradient	.01	0	.05
Porosity	.25	.01	.40

Organic Fraction	.005	.0002	.01
Parameter: Half-Lives (hrs)	Mid-Range Values	Low Values	High Values
Benz: aerobic	672	240	2500
Tol: aerobic	420	168	672
EB: aerobic	1440	144	2700
Xyl: aerobic	504	336	672
Benz: anaerobic	9984	2688	17280
Tol: anaerobic	3192	1344	5040
EB: anaerobic	4848	4224	5472
Xyl: anaerobic*	4656	672	12688

* Note: Anaerobic xylene values are taken for meta-xylene; aerobic values are constant for xylene isomers.

Because the dynamic model is structured to calculate concentrations of contaminant throughout the biodegradation process, the measure of model sensitivity was the change in computed concentration of total BTEX at an established time. The dynamic model software computed the biodegradation efficiently up to 75 days. Using a time step of 0.5 day and a section length of one foot, the parameters were altered according to their range values. One parameter was changed at a time and all other parameters were held at their mid-range value. The only exceptions were the half-lives/decay constants. To see the maximum effect of the electron acceptor concentrations on the dynamic model, half-lives were set at their lowest values (highest values as decay constants). To remain consistent when investigating the other parameters, the half-lives were held at their low levels. Table 11 below shows the percent change in total BTEX at 75 days, given the parameter and range value indicated.

Table 11. Sensitivity Analysis Results:

Percent change in BTEX at 75 days

Variable	O2	NO3	MnO2	Fe(OH)3	SO4
Low #:	2.9	0	0	0	0
Mid #:	0	0	0	0	0
High #:	-0.7	0	0	0	0

Variable	Hyd. Cond.	Porosity	Organic %	Hyd. Grad.
Low #:	47	0	0	0
Mid #:	0	0	0	0
High #:	0	0.4	0	0

Variable	Benz: aerob	Tol:aerob	EB:aerob	Xyl:aerob
Low #:	-0.4	0	-0.1	-0.06
Mid #:	0	0	0	0
High #:	0.4	0	0	0.06

Variable	Benz: anaerob	Tol: anaerob	EB: anaerob	Xyl: anaerob
Low #:	-18	-18	-0.4	-13.2
Mid #:		0	0	0
High #:	3.4	6.8	0.3	3.1

The most interesting effect observed is the lack of influence by the a[illegible]obic electron acceptor quantities. Also, the anaerobic half-lives have a far greater effect on the dynamic model than the quantity of the anaerobic electron acceptors. The conclusion follows that this research may not derive a significant relationship between the time of degrade BTEX compounds and the quantities of individual anaerobic electron acceptors.

However, further investigation of the model revealed that the absence of any anaerobic electron acceptors in the model resulted in a 99.4% increase in total BTEX after 75 days. The cumulative absence of anaerobic electron acceptors does affect contaminant concentrations, especially within the anaerobic core of the plume. It follows above a certain level, the total quantity of anaerobic electron acceptors will not affect the results of the dynamic plume model. Below this level, the quantity of electron acceptors does limit the biodegradation simulated in the model and thus affects model results. The model was briefly analyzed to find this level of anaerobic electron acceptors for certain BTEX levels. Results of this analysis are shown in Table 12.

Table 12. Electron Acceptor Levels Which Begin to Affect Model at Given Initial Levels of BTEX

BTEX (ppm)	20	33	40	50
EA (ppm)	21.06	30.78	39.69	50.22

The value for EA is a cumulative concentration for all four anaerobic electron acceptors. Nitrate and sulfate made up the bulk of these cumulative figures as the other acceptors were held at 5 ppm each. When manganese and iron were at their maximum values with nitrate and sulfate near zero, this influence point was not reached given a BTEX level of 33 ppm. This is not surprising as Mn (IV) and Fe (III) have low contaminant to acceptor mass ratios. Therefore, it seems that a minimum amount of nitrate or sulfate may need to be input into the model even with high values of iron or manganese in order to reach this point where the anaerobic electron acceptors no longer affect the results of the dynamic model.

Model Limitations. After implementing the dynamic degradation model with Quattro Pro v5.0 software, some limitations were observed. With section length values up to 1 ft, the total length of plume that can be characterized is limited to approximately 44 ft with the worksheet size limitations. Also, a single spreadsheet file could efficiently

accomplish calculations up to 150 time steps. Longer times required the linking of files and continuing the simulation. Though the software was capable of these functions, the size of each file made the process of simulating with multiple files a restrictively long process. One file with 150 time steps required 17 Mb of disk and RAM space. Computation time required only 15 to 20 seconds, yet transferring to secondary files to continue model simulation took over 30 minutes per transfer.

Correspondingly, the unanticipated results from the sensitivity analysis with regard to the anaerobic electron acceptors indicated that the initial methodology would not fully accomplish the goals of this research. These factors encouraged a probe into other viable characteristics about biodegradation plumes that could be used to predict the approximate time of biodegradation. This probe resulted in the analysis of the aerobic front and its movement through a plume.

V. Intrinsic Bioremediation Prediction Results

Aerobic Front Analysis

Key Parameters. The parameters which will most affect the velocity of the aerobic front are BTEX concentration (BTEX), oxygen concentration (O2), relative velocity of the ground water moving into the plume (Vrel) and the aerobic decay constants for the contaminants. The decay constants ca..ived from a single site assessment; therefore the mid-range decay constants were used. Table 13 shows the respective values used for the other three parameters.

Table 13. Range of Parameter Values to Characterize Aerobic Front

Parameter	Values Used
Total BTEX (ppm)	20, 33, 40, 50
Dissolved O2 (ppm)	2, 2.5, 3, 3.5, 4, 5
Relative Velocity (ft/d)	0.05, 0.1, 0.5, 0.76, 1.0, 1.5

Simulation Results. The simulations were run with one variable altered and the others held constant. Appendix II shows the results of this simulation. The simulation data was compiled such that the aerobic front contours could be defined and the aerobic front position at 4 ppm benzene identified. A contour is a plot of benzene concentrations through the center of the plume at a given time. Six contours can be plotted on one graph, as shown in Figure 18, which provide adequate data points with which to define the aerobic front positions through time.

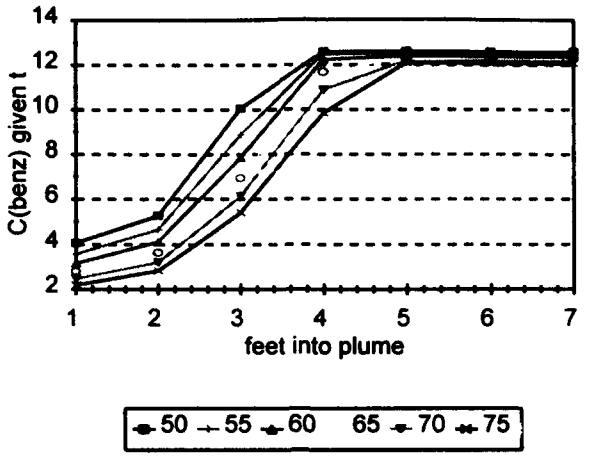

Figure 18. Aerobic Front contour lines. Benzene concentrations over length of plume at 50 to 75 days.

The positions of the aerobic front in Figure 18 plotted over time indicate the movement of the front given one set of input values from BTEX, O2 and Vrel. Figure 19 shows this data.

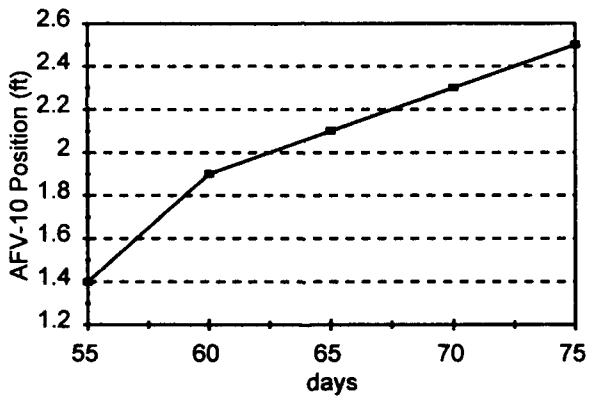

Figure 19. Aerobic Front Position over Time as defined at 10 ppm BTEX (4 ppm Benzene).

The movement of the aerobic front is relatively constant in this plot. The plots in appendix II, Section A, show the change in position verses time is somewhat constant through 150 days. Therefore, this research will consider the aerobic front velocity to be constant for given input parameters and that this velocity can be characterize in terms of the three input parameters.

The aerobic front velocity (AFV10) was defined for each data set according to its trend up to 75 days of biodegradation. The data was collected by altering one parameter at a time and the results are shown in Tables 14, 15 and 16 for each the three parameters.

Table 14: AFV10 Values for Input Parameters:

O2 = 4 ppm; Vrel = 1.0 ft/d (day); BTEX variable

BTEX (ppm):	20	33	40	50
AFV10 (ft/d)	0.068	0.04	0.04	0.025

Table 15: AFV10 Values for Input Parameters:

O2 = 4 ppm; BTEX = 33 ppm; Vrel variable

V.rel (ft/d)	0.05	0.11	0.5	0.76	1.0	1.5
AFV10 (ft/d)	0.0015	0.005	0.025	0.0325	0.035	0.053

Table 16: AFV10 Values for Input Parameters:

BTEX = 33 ppm, Vrel = 0.5 ft/d; O2 variable

O2 (ppm)	2	2.5	3	3.5	5
AFV10 (ft/d)	0.01	0.012	0.015	0.02	0.025

Aerobic Front Velocity Predictor. The above values were combined in a regression analysis to determine if a viable general linear model can be constructed with the aerobic front velocity (AFV10) as the dependent variable. The predictors in this model were the parameters BTEX, O2 and Vrel along with the square of these three parameters. The values were compiled and a stepwise regression with forward selection

was performed using STATISTIX v4.0. The stepwise regression procedure with forward selection evaluates each predictor and computes its contribution to estimating the dependent variable based on a least squares regression of the data. The contributions of each predictor are compared and a final model is selected that best estimates the dependent variable with as few predictors as possible. The test statistic used for predictor comparisons is the F-statistic generated from the least squares fit of each predictor. Results of this forward stepwise regression is shown in Table 17.

Table 17. Resulting Stepwise Model of AFV10

VARIABLE	COEFFICIENT	STD ERROR	STUDENT'S T	P	VIF
CONSTANT	0.09871	0.04988	1.98	0.0760	
BTX	-0.00685	0.00246	-2.78	0.0196	33.3
O2	0.01049	0.00360	2.91	0.0156	1.1
VREL	0.02946	0.00699	4.21	0.0018	1.1
BTX2	8.069E-05	3.417E-05	2.36	0.0398	33.5

CASES INCLUDED	15	R SQUARED	0.8001	MSE	9.146E-05
MISSING CASES	0	ADJ R SQ	0.7202	SD	0.00956

VARIABLES NOT IN THE MODEL

	CORRELATIONS		
VARIABLE	MULTIPLE	PARTIAL	T
OSQ	0.9906	-0.4875	-1.67
VREL2	0.9487	0.0783	0.24

This general linear model can be summarized as the following.

$$AFV10=0.099-0.007*BTEX+0.010*O2+0.029*Vrel+8.1E\text{-}5*BTEX^2$$

A test of the AFV10 predictor equation was performed in three cases. In each case, the input parameters are used to obtain the AFV10 value from the predictor equation and also used in running the dynamic plume simulation model and the aerobic front velocity found by charting the resulting data. The values obtained in the AFV10 predictor equation were compared to the corresponding value from the charted data. The test case would pass if the 95% prediction interval of the AFV10 predictor equation value included the value computed from the charted data.

In each test case, the inputs for the three parameters were selected to obtain combinations of values that were not used in the simulations for developing the AFV10 predictor equation. Also, the author wished to examine the accuracy of the predictor equation with parameter inputs that are near the bounds of the parameter values used in the simulations used to develop the equation. Test case 1 received a high BTEX and low Vrel input while test case 3 used a low BTEX and a high Vrel input. Test case 2 used middle range values for each parameter.

Test Case 1. The initial input values were: Total BTEX = 45 ppm, relative velocity of ground water (V.rel) = 0.4 ft/d and O2 = 3.5 ppm. The graphs derived from the simulation data are shown in Figures 20 and 21 along with the computed AFV10 value of 0.014 ft/d.

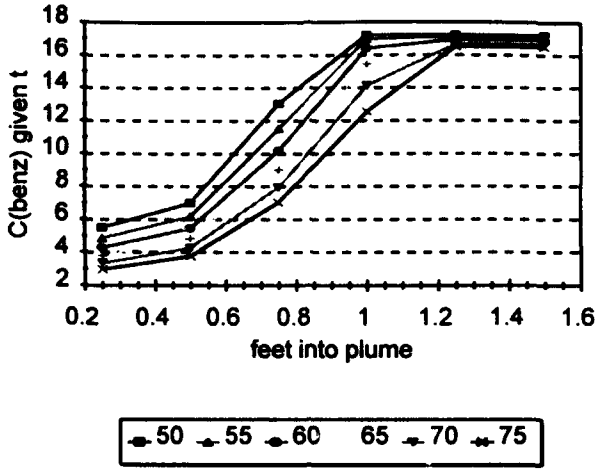

Figure 20. Test Case 1 AFV contours.

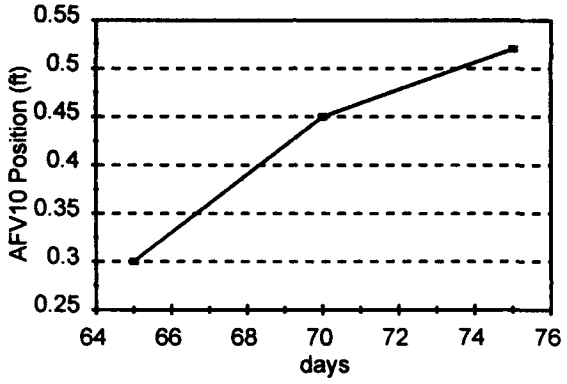

Figure 21. Test Case 1 AFV10 position vs time.

AFV10 = 0.014

The 95% prediction interval from the prediction equation of AFV10 using the above parameter values is shown in Table 18.

Table 18. Predicted/Fitted Values of AFV10, Test 1

LOWER PREDICTED BOUND	-0.0238	LOWER FITTED BOUND	-0.0130
PREDICTED VALUE	2.549E-03	FITTED VALUE	2.549E-03
UPPER PREDICTED BOUND	0.0289	UPPER FITTED BOUND	0.0181
SE (PREDICTED VALUE)	0.0118	SE (FITTED VALUE)	6.998E-03
UNUSUALNESS (LEVERAGE)	0.5354		
PERCENT COVERAGE	95.0		
CORRESPONDING T	2.23		

PREDICTOR VALUES: BTX = 45.000, BTX2 = 2025.0, O2 = 3.5400, VREL = 0.4000

The 95% prediction interval is [-0.0238, 0.0289]. Comparing the value obtained from the simulation of 0.014 ft/d, we see that the prediction interval does capture this value. However, the predicted value of 0.014 is about 5 times less than the simulation value.

Test Case 2. Input values: BTEX = 30 ppm, V.rel = 0.6 ft/d and 0@ = 3 ppm. The simulation plots are shown in Figures 22 and 23. The computed AFV10 is 0.025 ft/d.

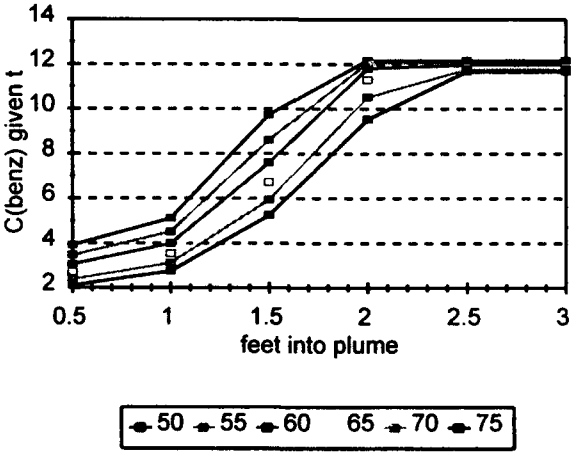

Figure 22. Test Case 2 AFV Contours.

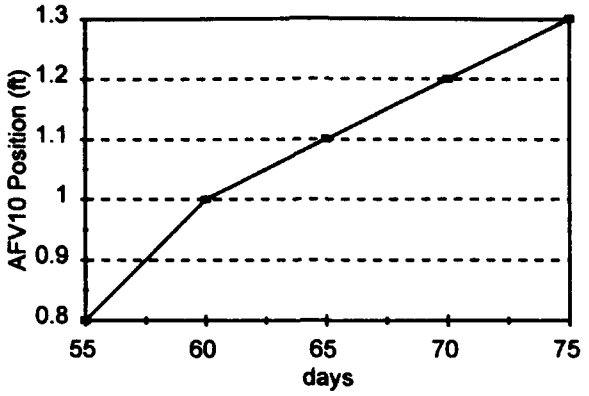

Figure 23. Test Case 2. AFV10 Position vs Time.
AFV10 = 0.025 ft/d

The predictor equation gives us the 95% prediction interval as seen in Table 19.

Table 19. Predicted/Fitted Values of AFV10, Test 2

LOWER PREDICTED BOUND	-8.658E-03	LOWER FITTED BOUND	4.950E-03
PREDICTED VALUE	0.0148	FITTED VALUE	0.0148
UPPER PREDICTED BOUND	0.0383	UPPER FITTED BOUND	0.0247
SE (PREDICTED VALUE)	0.0105	SE (FITTED VALUE)	4.434E-03
UNUSUALNESS (LEVERAGE)	0.2150		
PERCENT COVERAGE	95.0		
CORRESPONDING T	2.23		
PREDICTOR VALUES: BTX = 30.000, BTX2 = 900.00, O2 = 3.0000, VREL = 0.6000			

The 95% prediction interval is [-0.0086, 0.038] which does capture the simulation value of 0.025 ft/day and the predicted value is within 40% of the simulation value.

Test Case 3. Input values are: BTEX = 25 ppm, V.rel = 1.2 ft/d, O2 = 2.6 ppm. Graphs from simulation are shown in Figures 24 and 25. The computed AFV10 is 0.048 ft/d.

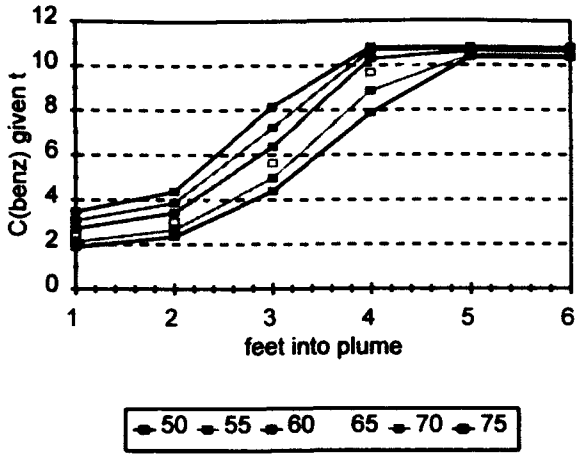

Figure 24. Test Case 3 AFV Contours.

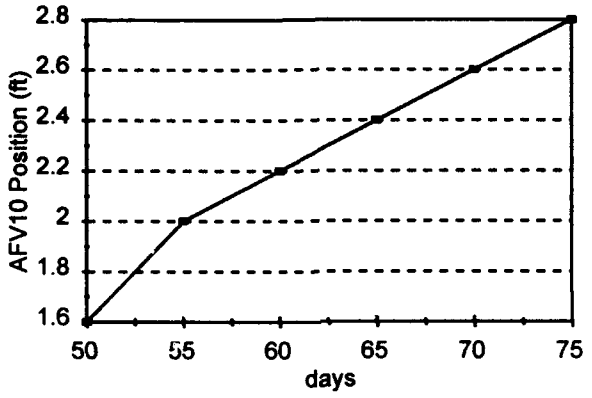

Figure 25. Test Case 3 AFV10 Position vs Time.
AFV10 = 0.048 ft/d

Table 20 shows the 95% prediction interval from the AFV10 equation.

Table 20. Predicted/Fitted Values of AFV10, Test 3.

LOWER PREDICTED BOUND	0.0142	LOWER FITTED BOUND	0.0251
PREDICTED VALUE	0.0404	FITTED VALUE	0.0404
UPPER PREDICTED BOUND	0.0665	UPPER FITTED BOUND	0.0556
SE (PREDICTED VALUE)	0.0117	SE (FITTED VALUE)	6.826E-03
UNUSUALNESS (LEVERAGE)	0.5095		
PERCENT COVERAGE	95.0		
CORRESPONDING T	2.23		

PREDICTOR VALUES: BTX = 25.000, BTX2 = 625.00, O2 = 2.6000, VREL = 1.2000

The 95% prediction interval is [0.0142, 0.0665] which does capture the simulation value for AFV10 of 0.048 ft/d. The predicted value is a close match to the simulation value.

Application of Field Data

The model constructed is intended to provide a prediction of intrinsic bioremediation based on theoretical biodegradation. Parameters were designed and assumptions were made to produce a conservative model. Results from this model should be a less favorable outcome compared to the expected realistic outcomes of intrinsic bioremediation performance. This section of the research will describe the conclusions of the work as related to its intended application to real world data.

Inserting Site Data. Based on a conservative estimate of intrinsic bioremediation performance, the characterization of the aerobic front through the plume should yield a reasonable, yet conservative estimate of intrinsic bioremediation duration. Three examples of using the AFV10 predictor equation to indicate intrinsic bioremediation duration were compiled. Example 1 used a moderate BTEX value and moderate ground

water velocity (see Table 21). Example 2 used a low BTEX input and a low/moderate ground water velocity (see Table 22). Example 3 used a moderate BTEX and a low/moderate ground water velocity (see Table 23).

Table 21. Example 1 Application of AFV10 Predictor

Site Data:			
Benzene=	16.5ppm	Hyd Cond=	30.00ft/d
Toluene=	16ppm	Hyd Grad=	0.01
E.Benz=	2.5ppm	porosity=	0.25
Xylenes=	5ppm	organic	
Total BTEX:	40ppm	fraction=	0.01
O2=	4ppm	Retard =	4.09
		Vel.gw=	1.20ft/d
Plume		Vel.c=	0.29ft/d
Length=	150ft	Vel.rel=	0.91ft/d
Prediction Model:	Aerobic Front Velocity=		0.02ft/d
	Time for front to travel in plume =		6662.78days
			18.25years
	Distance plume migrates=		1956.96ft
			0.37miles

Table 22. Example 2 Application of AFV10 Predictor

Site Data:			
Benzene=	12ppm	Hyd Cond=	20.00ft/d
Toluene=	10ppm	Hyd Grad=	0.01
E.Benz=	1.5ppm	porosity=	0.25
Xylenes=	3.5ppm	organic	
Total BTEX:	27ppm	fraction=	0.01
O2=	4ppm	Retard =	4.09
		Vel.gw=	0.80ft/d
Plume		Vel.c=	0.20ft/d
Length=	150ft	Vel.rel=	0.60ft/d
Prediction Model:	Aerobic Front Velocity=		0.03ft/d
	Time for front to travel in plume =		4632.14days
			12.69years
	Distance plume migrates=		907.02ft
			0.17miles

Table 23. Example 3 Application of AFV10 Predictor

Site Data:			
Benzene=	20ppm	Hyd Cond=	20.00ft/d
Toluene=	18ppm	Hyd Grad=	0.01
E.Benz=	3ppm	porosity=	0.25
Xylenes=	5ppm	organic	
Total BTEX:	46ppm	fraction=	0.01
O2=	4ppm	Retard =	4.09
		Vel.gw=	0.80ft/d
Plume		Vel.c=	0.20ft/d
Length=	150ft	Vel.rel=	0.60ft/d
Prediction Model:	Aerobic Front Velocity=		0.01ft/d
	Time for front to travel in plume =		10601.11days
			29.04years
	Distance plume migrates=		2075.81ft
			0.39miles

Given site conditions as shown, three different AFV10 values were obtained. The plume length was held constant for each case so the impact of the aerobic front velocity

on the time to degrade would be observed. The time estimates of degradation for these examples ranged from 12.7 years to 29 years for the same size plume

Additional Considerations. In considering a large plume for a site, the use the AFV10 predictor equation to forecast intrinsic bioremediation duration may be extremely conservative. With a plume length of several hundred feet, the time for the front to reach the far end of the plume may seem unreasonably high. In actuality, the influence of the anaerobic degradation should allow a large plume to degrade in less time than the aerobic degradation and aerobic front velocity will indicate. The time for the anoxic portion of the plume to anaerobically degrade can be estimated from the published decay constants. Considering the anaerobic degradation of benzene, the estimated time for anaerobic biodegradation to deplete the BTEX is found by:

$$t_{anaerob}=\ln(4/Po)*(-600.2)$$

where t.anaerob is given in days. When applying actual site data and the time computed for anaerobic biodegradation is less than the time for the aerobic front to move through the plume, then perhaps the anaerobic degradation will be a significant process at this site. An example of how this may occur is displayed in Table 24.

Table 24. Comparison of Aerobic Decay Influence vs Anaerobic Decay

Aerobic Front velocity (typical) 0.03ft/d	Anaerobic decay: Initial BTEX 40ppm
Plume Length 40ft	
Time to degrade (via aerobic front) 1333.33days or 3.65years	Time to degrade 1382.01days or 3.79years
Distance of travel (if V.plume=0.2ft/d) 266.67ft or 0.05miles	Distance of travel 276.40ft or 0.05miles
Note: anaerobic decay appears to occur to the leading edge of plume to a distance of 250 ft. (given EAs equal 75 ppm, btex=40, Vrel=0.5ft/d)	
Aerobic Front velocity (typ) 0.03ft/d	Anaerobic decay: Initial BTEX 40ppm
Plume Length 250ft	
Time to degrade (via aerobic front) 8333.33days or 22.83years	Time to degrade 1382.01days or 3.79years
Distance of travel (if V.plume=0.2ft/d) 1666.67ft or 0.32miles	Distance of travel 276.40ft or 0.05miles

This example shows a case where a 40 foot plume is dominated by aerobic biodegradation. However, anaerobic decay appears to overshadow the 250 foot plume by

indicating that the time of degradation may be as short as 3.8 years compared to the 22.8 years for aerobic degradation. Given different input values, the point where anaerobic degradation becomes more of an influence than aerobic degradation will change. This data demonstrates the influence of anaerobic decay on larger plumes and a need to be able to characterize anaerobic biodegradation in order to make accurate predictions of intrinsic bioremediation duration in these larger plumes.

VI. Conclusions and Recommendations

Review of Significant Findings

Static Plume. The analysis of the static plume indicated that, with a mid-range loading of electron acceptors, about 10 ppm of total BTEX could be degraded by microorganisms. If the electron acceptors were at their maximum observed values, then the total BTEX degraded could be up to 30 ppm. With BTEX loadings above 30 ppm, it is improbable that an aquifer has adequate electron acceptors to degrade the plume without significant quantities of ground water passing through the plume introducing additional electron acceptors.

Dynamic Plume. Sensitivity analysis revealed that anaerobic electron acceptors affected the performance of intrinsic bioremediation up to a certain level. If concentrations of these electron acceptors were above this level, then the quantity of these electron acceptors no longer influenced the performance of intrinsic bioremediation. A brief assessment of these levels show them to be near equivalent to the respective initial BTEX loadings. The concept of predicting the duration of intrinsic bioremediation using the quantity of anaerobic electron acceptors was discarded in favor of predicting this duration by characterizing the movement of aerobic ground water through the plume.

Aerobic Front. The motion of the aerobic front was observed through the simulated plumes up to 150 days and this motion appeared to be relatively constant given a fixed set of input parameters. This front velocity was characterized with changing BTEX loadings, dissolved oxygen concentrations and relative velocity of ground water moving into the plume. A regression was performed on this simulation data and a general linear model developed that predicted the velocity of the front. The relative ground water velocity was the parameter that contributed the most to the AFV10 prediction equation.

Discussion of Methodology Error

Simulation Model Concept. The model was created with the intent to simplify the intrinsic bioremediation process. Uncertainties such as contaminant decay constants were researched and values assigned. Other assumptions were made to devise a conservative simulation of intrinsic bioremediation. Key sources of error in this model include the assignment of decay constants, assumption of acclimated microorganisms and characterizing the microbiological process of biodegradation as a simple mass balance. The decay constants appear to be highly variable with no published method to adjust the decay constant for specific site conditions. The mass balance approximation of biodegradation may derive error from the fact that the degradation of hydrocarbons occurs in many steps along the pathway to the end product such as carbon dioxide. The assumptions made were necessary to develop a straightforward simulation of intrinsic bioremediation that a few significant parameters could significantly influence.

Conclusions were derived from the relative impact of parameters on the entire intrinsic bioremediation process. Therefore, the actual computed values of BTEX concentration were not as critical as how the these biodegradation values changed with the change in parameters. Because the errors inherent in the calculated BTEX concentrations should be consistent throughout the simulations, these errors should not pose a major impact on drawing conclusions from the sensitivity analysis or aerobic front analysis.

Considering a macroscopic view of intrinsic bioremediation duration, the range of possible values is quite large. Complete intrinsic bioremediation could take only a few months up to even a decade or more. The uncertainty in these simulations, aerobic front velocity prediction and resulting prediction of remediation duration could give a duration prediction that is several months or more off from the actual intrinsic bioremediation

duration. For large plumes over 1000 ft long, perhaps the predicted duration would be a year or two in error from the actual time. Yet, large plumes should take several years to degrade so this error may not be profound. The significance of the model error should be a factor for those sites where the prediction of degradation time is sensitive within to a few months or less. The error would also be significant for a site where the distance a plume could move without concern is limited to within one hundred feet.

Aerobic Front Velocity Prediction Result. Assuming the values obtained from the dynamic plume simulations are within acceptable bounds to actual intrinsic bioremediation performance, the aerobic front velocity prediction in the form of a general linear model contains some measurable error. The coefficient of multiple determination, noted by the R^2 value, for the regression was 80% which indicated that 20% of the variance in the aerobic front velocities could not be explained by the four predictor variables used (Neter and others, 1989: 241). This R^2 number appears adequate for a simple prediction of the aerobic front velocity with the true measure of this suitability being the accuracy of the prediction compared against real site data. The author also makes allowances that future work to continue characterizing aerobic front values could produce a more exact AFV10 prediction equation.

Recommendations for Further Research

Improvements to Thesis Methodology. A number of different approaches could be undertaken to accomplish the same intent achieved in this research work. The dynamic plume model could be reused with new conclusion derived on intrinsic bioremediation performance analyzing other aspects than aerobic front movement. Other models can be utilized to simulate the conditions analyzed in this work to characterize plume intrinsic bioremediation. For example, AFCEE has recently contracted for the development of BIOPLUME III which will simulate anaerobic degradation. The same

dynamic plume model can also be constructed using different software that would not be memory intensive. Mathcad or Matlab may be adequate to compute the same biodegradation algorithms and do so with a time dependent variable.

Validation of Intrinsic Bioremediation Prediction Model. It is the hope of the author that the results and conclusions derived from this research work may be applied to real site conditions and validated as representative of actual intrinsic bioremediation. The computations of the simple and dynamic plume models as well as the AFV10 prediction equation must be validated against actual site data and its accuracy determined through hypothesis testing before it can be applied. It is also the author's hope that once this validation is complete that the information will be compiled into a format that could be used in decision models concerning remediation avenues at actual contamination sites.

Possible sources for obtaining real site data would be AFCEE, the Environmental Management Directorate at Wright-Patterson AFB and also the Department of Geological Sciences at Wright State University.

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Appendix I: Characterization of JP-4

Table A1-1. Hydrocarbon Composition of JP-4

Compound	Mass %	Solubility (mg/L)	Mass factor
Benzene	.538	1780	9.576
Toluene	1.811	515	9.327
Xylenes	1.873	160	2.997
Ethylbenzene	.797	160	1.275
Cyclohexane	.97	55	0.534
Naphthalene	.30	32	0.096
Butane	.32	61	0.195
Pentane	.82	42	0.344
2-Methylbutane	.98	48	0.470
2-Methylpentane	2.41	14	0.337
3-Methylpentane	2.01	13	0.261
Methylcyclopentane	.84	42	0.353
2,2,3-Trimethylbutane	.07	48	0.034
2-Methylhexane	5.14	4	0.206
2,3-Dimethylpentane	1.88	20	0.376
3-Methylhexane	6.63	3	0.199
3-Ethylpentane	.93	20	0.186
2,2,4-Trimethylpentane	.11	14	0.015
Methylcyclohexane	1.0	14	0.140
2,2-Dimethylhexane	.47	3	0.014
Ethylcyclopentane	.22	160	0.352
2,5-Dimethylhexane	.79	3	0.024
2,4-Dimethylhexane	1.15	3	0.035
3,3-Dimethylhexane	.36	3	0.011
2,3-Dimethylhexane	.8	3	0.024
2,3,4-Trimethylpentane	.15	14	0.021
2-Methylheptane	2.86	1	0.029
4-Methylheptane	1.36	1	0.014
3-Methylheptane	3.45	1	0.035
3-Ethylhexane	.95	4	0.038
1,3-Dimethylcyclohexane	.4	6	0.024
1,1-Dimethylcyclohexane	.1	6	0.006
1,2-Dimethylcyclohexane	.14	4	0.006
2,2-Dimethylheptane	.14	1	0.001
2,4-Dimethylheptane	.24	1	0.002
2,6-Dimethylheptane	.16	1	0.002

2,5-Dimethylheptane	.43	1	0.004
3,3-Dimethylheptane	.13	1	0.001
2,3-Dimethylheptane	.31	1	0.003
1,2,4-Trimethylcyclohexane	.09	1	0.001
4-Methyloctane	.55	0.1	0.001
3-Methyloctane	.72	0.1	0.001
1-Ethyl,3-methylcyclohexane	.13	6	0.008
Cumene	.25	50	0.125
2,6-Dimethyloctane	.20	0.1	0.000
3,4-Diethylhexane	.24	4	0.010
1,3,5-Trimethylbenzene	.47	48	0.226
1,2,4-Trimethylbenzene	1.58	52	0.822
4-Ethyloctane	.15	0.6	0.001
1-Ethyl,2-methylbenzene	.49	75	0.368
2-Methylnonane	.20	0.1	0.000
3-Methylnonane	.18	0.1	0.000
Isobutylbenzene	.07	17	0.012
3-Ethylnonane	.07	0.1	0.000
1-Methyl,3-isopropylbenzene	.13	62	0.081
Indan	.08	109	0.087
Butylcyclohexane	.08	14	0.011
1-Methyl,3-propylbenzene	.26	60	0.156
1,4-Diethylbenzene	.24	160	0.384
Butylbenzene	.15	14	0.021
1-Methyl,2-propylbenzene	.20	60	0.120
4-Methyldecane	.35	0.1	0.000
1,4-Dimethyl,4-ethylbenzene	.41	160	0.656
1,3-Dimethyl,3-ethylbenzene	.30	160	0.480
1,2-Dimethyl,4-ethylbenzene	.45	160	0.720
1,2-Dimethyl,3-ethylbenzene	.17	160	0.272
2-Methyldecane	.24	0.1	0.000
1-Ethyl,3-isopropylbenzene	.09	62	0.056
1,2,3,5-Tetramethylbenzene	.39	4	0.016
2,6-Dimethyldecane	.16	0.1	0.000
Tetralin	.20	15	0.030
Pentylbenzene	.07	4	0.003
1,4-Di-isopropylbenzene	.21	60	0.126
2-Methylundecane	.20	0.1	0.000
1,2,4-Triethylbenzene	.1	160	0.160
Hexylbenzene	.14	1	0.001
2-Methylnapthalene	.21	25	0.053
1-Methylnapthalene	.17	28	0.048
Hexane	3.80	13	0.494

Heptane	7.22	3	0.217
Octane	3.19	0.6	0.019
Nonane	1.15	0.1	0.001
Decane	.97	0.1	0.001
Undecane	1.96	0.1	0.002
Dodecane	2.39	0.1	0.002
Tridecane	2.07	0.1	0.002
Tetradecane	1.40	0.1	0.001
Pentadecane	.60	0.1	0.001
Hexadecane	.17	0.1	0.000
Heptadecane	.05	0.1	0.000
Total	79.399 %		33.363

Key:
Mass % = average mass percentage of compound in JP-4 (Hayes and Pitzer, 1986)
Solubility = solubility of compound in water (MacKay and others, 1993)
Mass factor = relative dissolved mass factor of compound

Note: The mass % column doesn't sum to 100% because the remainder of JP-4 contains many compounds that individually contribute litte to the mass of JP-4

Table A1-2. Biodegradable Hydrocarbon Composition of JP-4.

Note: Those compounds determined to be not biodegradable, whether aerobic or anaerobic, are labeled with an asterisk (Mackay and others, 1992; Howard and others. 1991; Chapelle, 1993)

Compound	Mass %	Solubility (mg/L)	Mass factor x 100
Benzene	.538	1780	957.6
Toluene	1.811	515	932.7
Xylenes	1.873	160	299.7
Ethylbenzene	.797	160	127.5
Cyclohexane*	.97	55	--
Naphthalene	.30	32	9.6
Butane	.32	61	19.5
Pentane	.82	42	34.4
2-Methylbutane	.98	48	47.0
2-Methylpentane	2.41	14	33.7
3-Methylpentane	2.01	13	26.1
Methylcyclopentane*	.84	42	--
2,2,3-Trimethylbutane	.07	48	3.4
2-Methylhexane	5.14	4	20.6
2,3-Dimethylpentane	1.88	20	37.6
3-Methylhexane	6.63	3	19.9
3-ethylpentane	.93	20	18.6
2,2,4-Trimethylpentane	.11	14	1.5
Methylcyclohexane*	1.0	14	--
2,2-Dimethylhexane	.47	3	1.4
Ethylcyclopentane*	.22	160	--
2,5-Dimethylhexane	.79	3	2.4
2,4-Dimethylhexane	1.15	3	3.5
3,3-Dimethylhexane	.36	3	1.1
2,3-Dimethylhexane	.8	3	2.4
2,3,4-Trimethylpentane	.15	14	2.1
2-Methylheptane	2.86	1	2.9
4-Methylheptane	1.36	1	1.4
3-Methylheptane	3.45	1	3.5
3-Ethylhexane	.95	4	3.8
1,3-Dimethylcyclohexane*	.4	6	--
1,1-Dimethylcyclohexane*	.1	6	--
1,2-Dimethylcyclohexane*	.14	4	--
2,2-Dimethylheptane	.14	1	0.1

2,4-Dimethylheptane	.24	1	0.2
2,6-Dimethylheptane	.16	1	0.2
2,5-Dimethylheptane	.43	1	0.4
3,3-Dimethylheptane	.13	1	0.1
2,3-Dimethylheptane	.31	1	0.3
1,2,4-Trimethylcyclohexane*	.09	1	--
4-Methyloctane	.55	0.1	0.1
3-Methyloctane	.72	0.1	0.1
1-Ethyl,3-Methylcyclohexane*	.13	6	--
Cumene	.25	50	12.5
2,6-Dimethyloctane	.20	0.1	0.0
3,4-Diethylhexane	.24	4	1.0
1,3,5-Trimethylbenzene*	.47	48	--
1,2,4-Trimethylbenzene*	1.58	52	--
4-Ethyloctane	.15	0.6	0.1
1-Ethyl,2-Methylbenzene*	.49	75	--
2-Methylnonane	.20	0.1	0.0
3-Methylnonane	.18	0.1	0.0
Isobutylbenzene	.07	17	1.2
3-Ethylnonane	.07	0.1	0.0
1-Methyl,3-isopropylbenzene*	.13	62	--
Indan	.08	109	8.7
Butylcyclohexane*	.08	14	--
1-Methyl,3-propylbenzene*	.26	60	--
1,4-Diethylbenzene	.24	160	38.4
Butylbenzene	.15	14	2.1
1-Methyl,2-propylbenzene*	.20	60	--
4-Methyldecane	.35	0.1	0.0
1,4-Dimethyl,4-Ethylbenzene*	.41	160	--
1,3-Dimethyl,3-Ethylbenzene*	.30	160	--
1,2-Dimethyl,4-Ethylbenzene*	.45	160	--
1,2-Dimethyl,3-Ethylbenzene*	.17	160	--
2-Methyldecane	.24	0.1	0.0
1-Ethyl,3-isopropylbenzene*	.09	62	--
1,2,3,5-Tetramethylbenzene*	.39	4	--
2,6-Dimethyldecane	.16	0.1	0.0
Tetralin	.20	15	3.0
Pentylbenzene	.07	4	0.3
1,4-Di-isopropylbenzene*	.21	60	--
2-Methylundecane	.20	0.1	0.0
1,2,4-Triethylbenzene*	.1	160	--
Hexylbenzene	.14	1	0.1
2-Methylnapthalene	.21	25	5.3

1-Methylnapthalene	.17	28	4.8
Hexane	3.80	13	49.4
Heptane	7.22	3	21.7
Octane	3.19	0.6	1.9
Nonane	1.15	0.1	0.1
Decane	.97	0.1	0.1
Undecane	1.96	0.1	0.2
Dodecane	2.39	0.1	0.2
Tridecane	2.07	0.1	0.2
Tetradecane	1.40	0.1	0.1
Pentadecane	.60	0.1	0.1
Hexadecane	.17	0.1	0.0
Heptadecane	.05	0.1	0.0
Total	79.399 %		2,766.9

Determination of BTEX fraction of total biodegradable dissolved hydrocarbons:

Sum of BTEX mass factors = 2317.5
Sum of biodegradable mass factors = 2766.9
Unaccounted Hydrocarbons mass = 100 % - 79.4 % = 20.6 %
Estimated solubility of unaccounted mass: use average solubility of key aliphatics = (13 + 3 + 0.6 + 0.1)/4 = 4.18 mg/L
Unaccounted mass factor = 20.6 * 4.18 = 86.1
Total biodegradable mass factor = 2766.9+86.1 = 2853.0

BTEX fraction of total biodegradable hydrocarbons = 2317.5/2853.0 = 81.2%;
Use 81 %.

Appendix II. Simulation Data for Characterizing Aerobic Front

A. Summa AFV10 values from simulation data @ intersection of aerobic front with 4 ppm ben (10 ppm BTEX)

Table A2-1. Block 1: change in BTEX; Vrel=1.0, O=4

Btex: (ppm)	AFV10: (ft/d)
20	0.068
33	0.04
40	0.04
50	0.025

Table A2-2. B change in Vrel; BTEX=33, O=4

Vrel: (ft/	AFV10 (ft/d)
0.05	0.0015
0.11	0.005
0.5	0.025
0.76	0.0325
1	0.035
1.5	0.0533

Table A2-3. Block 3: change O2; Vrel=0.5, BTEX=33

O2: ppm	AFV10: (ft/d)
2	0.01
2.5	0.012
3	0.015
3.5	0.02
5	0.025

B. Evaluation of Aerobic Front (AFront) to Ensure Consistency to 150 days.
Data used: Vrel = 0.76 ft/d, BTEX = 33 ppm, O2 = 3.5 ppm

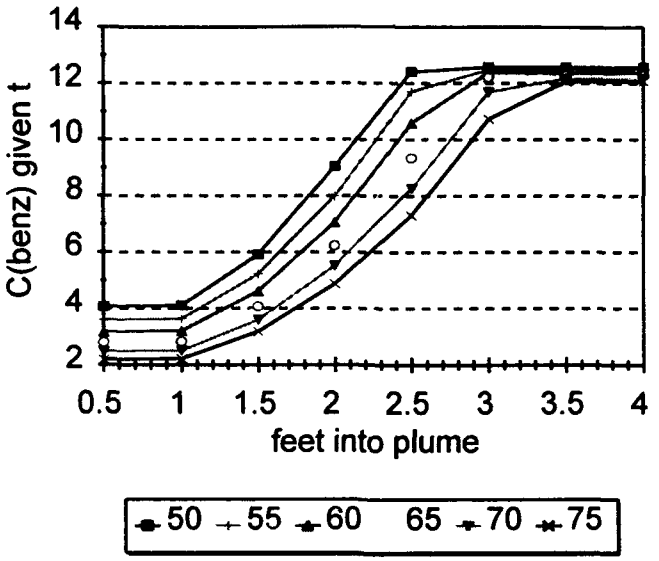

Figure A2-1. C(benz) over Plume Length. @ t = 50 to 75 days.

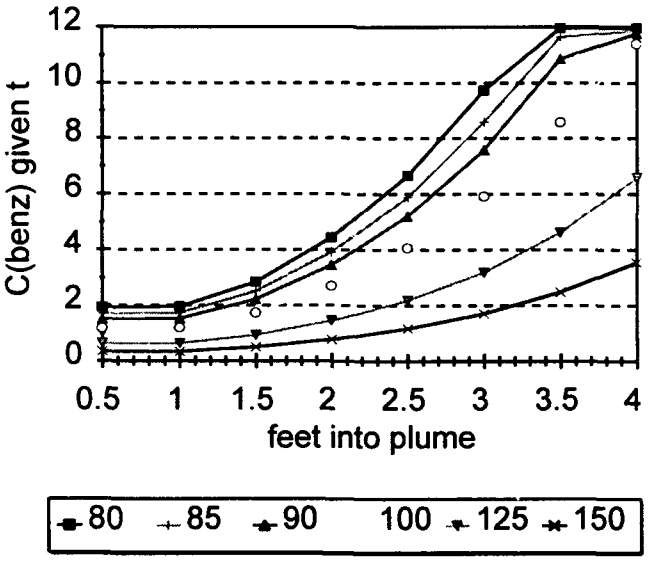

Figure A2-2. C(benz) over Plume Length. @ t = 75 days to 150 days.

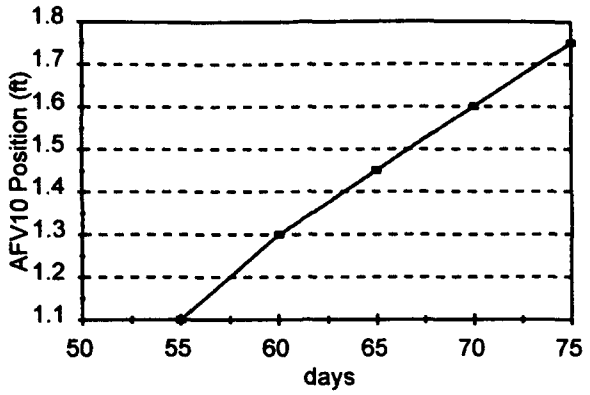

Figure A2-3. AFront Position over time. t = 50 to 75 days.

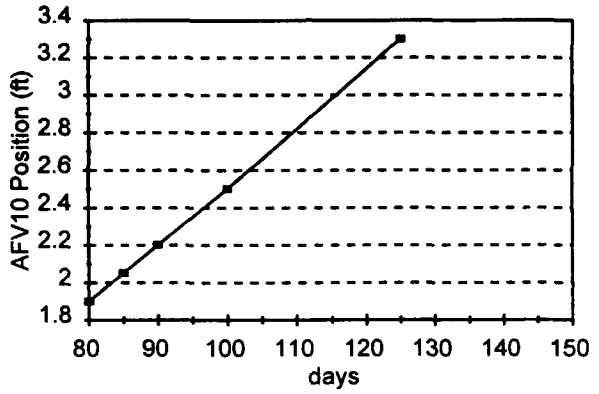

Figure A2-4. AFront Position over time. t = 75 to 150 days.

C. Evaluation of Aerobic Front to Ensure Consistency to 150 days.
Data used: Vrel = 1.0 ft/d, BTEX = 33 ppm, O2 = 2.5 ppm

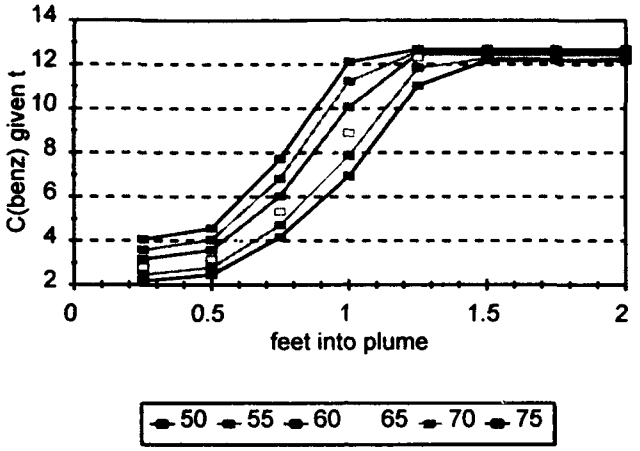

Figure A2-5. C(benz) over Plume Length. @ t = 50 to 75 days.

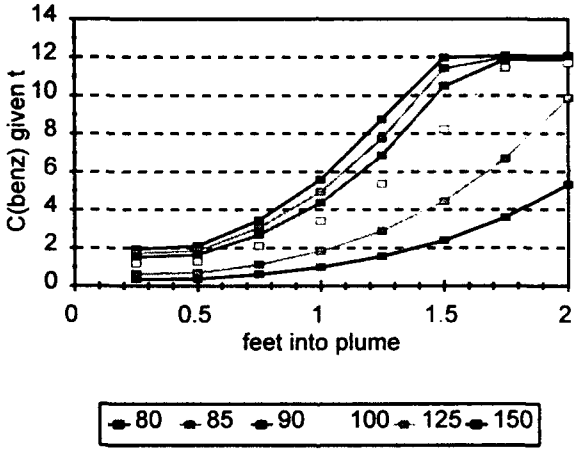

Figure A2-6. C(benz) over Plume Length. @ t = 75 days to 150 days.

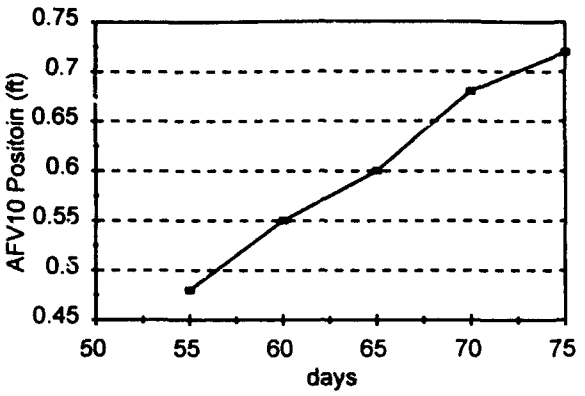

Figure A2-7. AFront Position over time. t = 50 to 75 days

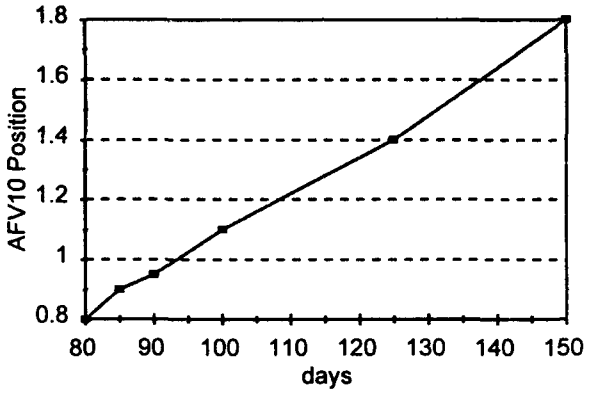

Figure A2-8. AFront Position over time. t = 75 to 150 days

D. Simulation Data with Variable BTEX, Vrel, O2 Values

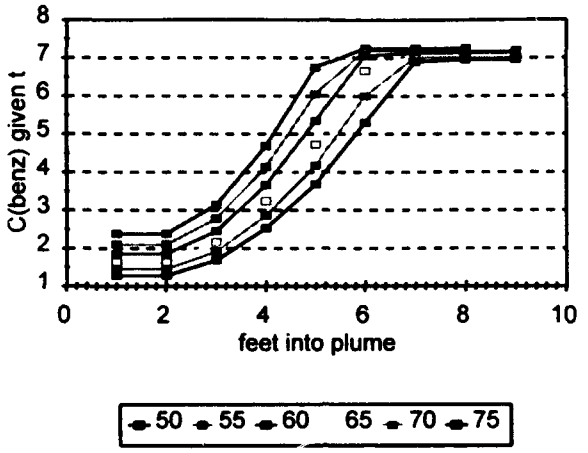

Figure A2-9. C(benz) over Plume Length, @ t = 50 to 75 days, with data:
BTEX = 20, Vrel = 1ft/d, O2 =4

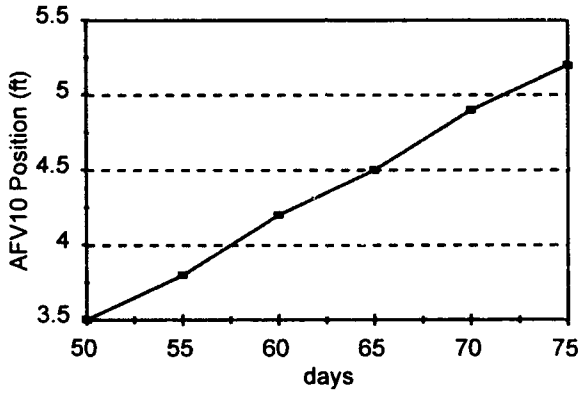

Figure A2-10. AFront Position over time to 75 days with data:
BTEX = 20, Vrel = 1ft/d, O2 =4

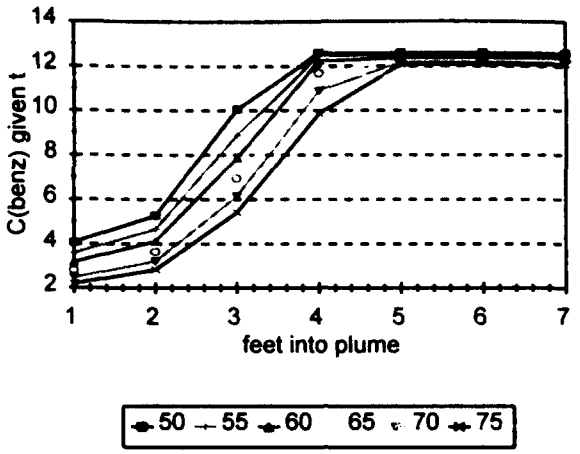

Figure A2-11 C(benz) over Plume Length, @ t = 50 to 75 days, with data: BTEX = 33, Vrel = 1ft/d, O2 =4

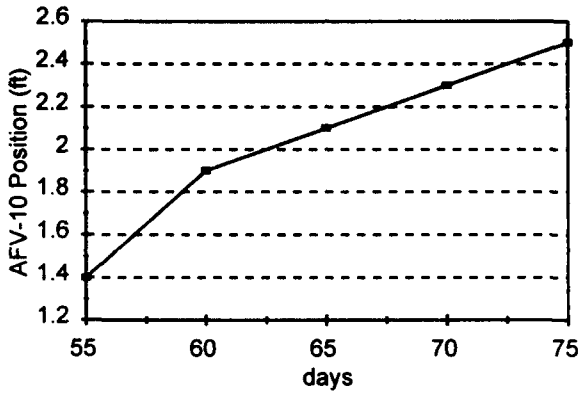

Figure A2-12. AFront Position over time to 75 days with data: BTEX = 33, Vrel = 1ft/d, O2 =4

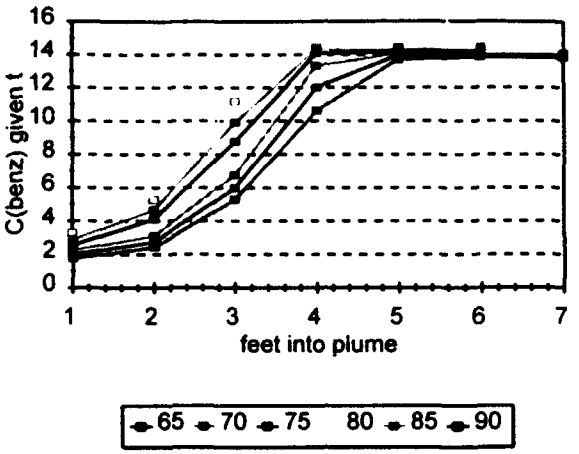

Figure A2-13 C(benz) over Plume Length, @ t = 50 to 75 days, with data:
BTEX = 40, Vrel = 1ft/d, O2 =4

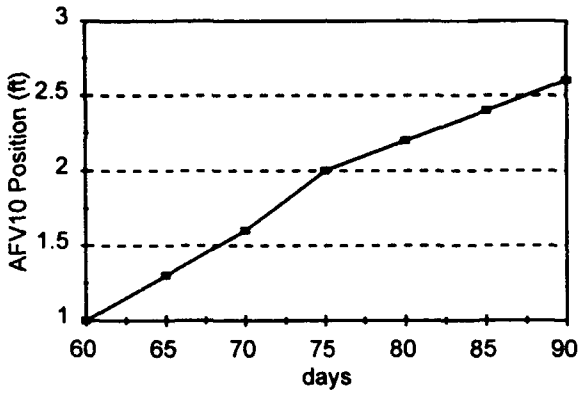

Figure A2-14. AFront Position over time to 75 days with data:
BTEX = 40, Vrel = 1ft/d, O2 =4

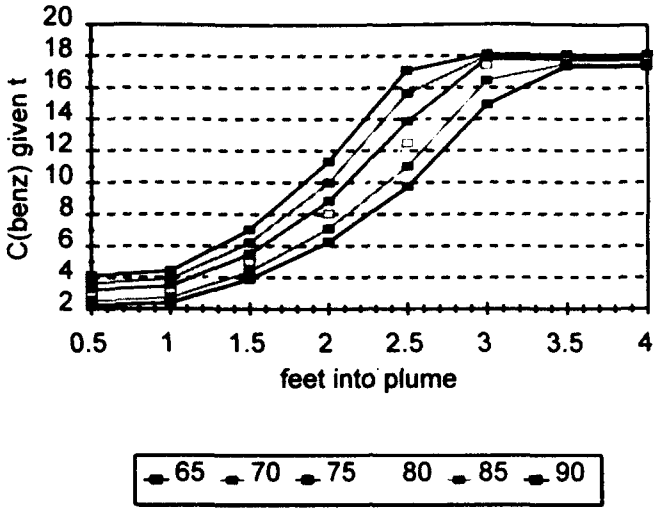

Figure A2-15 C(benz) over Plume Length, @ t = 50 to 75 days, with data:
BTEX = 50, Vrel = 1ft/d, O2 =4

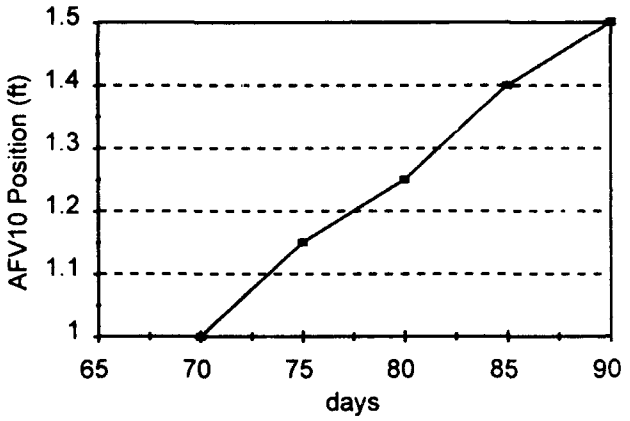

Figure A2-16. AFront Position over time to 75 days with data:
BTEX = 50, Vrel = 1ft/d, O2 =4

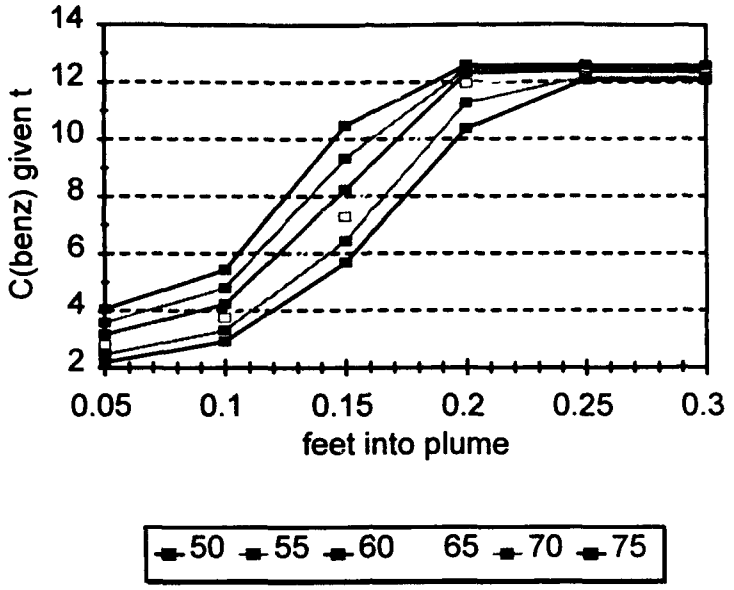

Figure A2-17 C(benz) over Plume Length, @ t = 50 to 75 days, with data:
Vrel = 0.05, BTEX = 33, O2 = 4

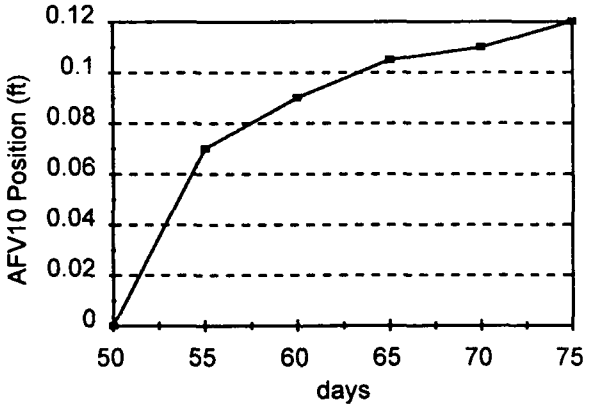

Figure A2-18. AFront Position over time to 75 days with data:
Vrel = 0.05, BTEX = 33, O2 = 4

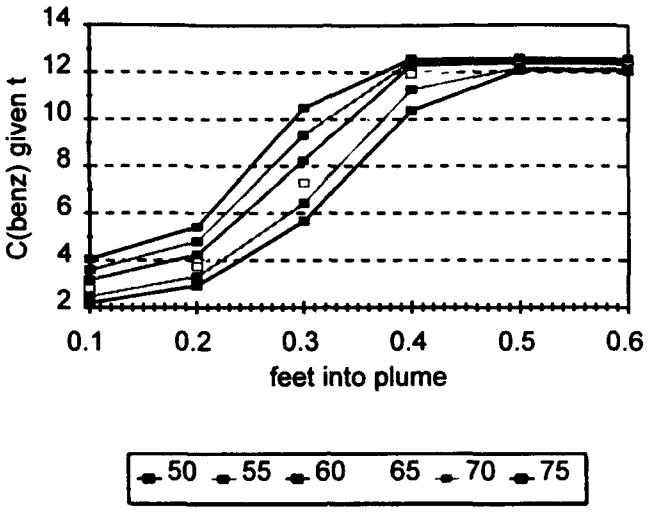

Figure A2-19 C(benz) over Plume Length, @ t = 50 to 75 days, with data:
Vrel = 0.1, BTEX = 33, O2 = 4

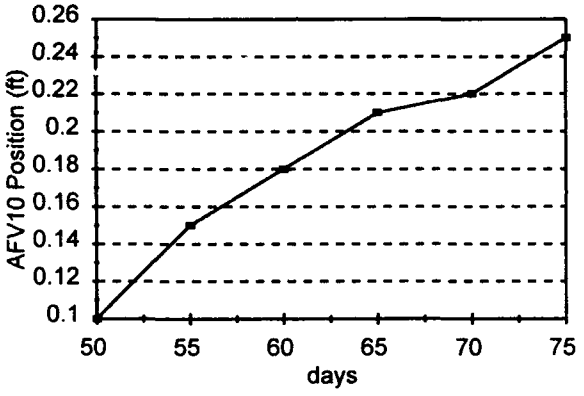

Figure A2-20. AFront Position over time to 75 days with data:
Vrel = 0.1, BTEX = 33, O2 = 4

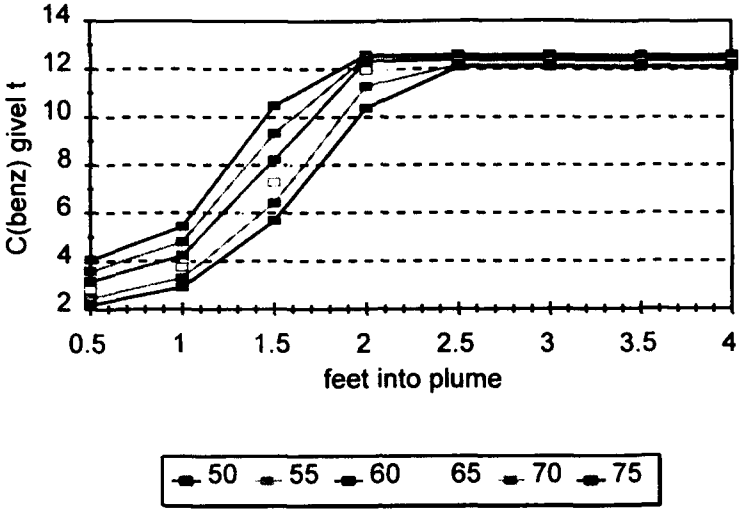

Figure A2-21 C(benz) over Plume Length, @ t = 50 to 75 days, with data: Vrel = 0.5 ft/d, BTEX = 33, O2 = 4

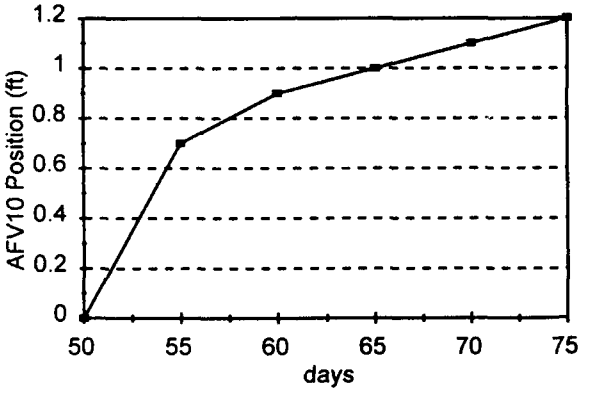

Figure A2-22. AFront Position over time to 75 days with data: Vrel = 0.5 ft/d, BTEX = 33, O2 = 4

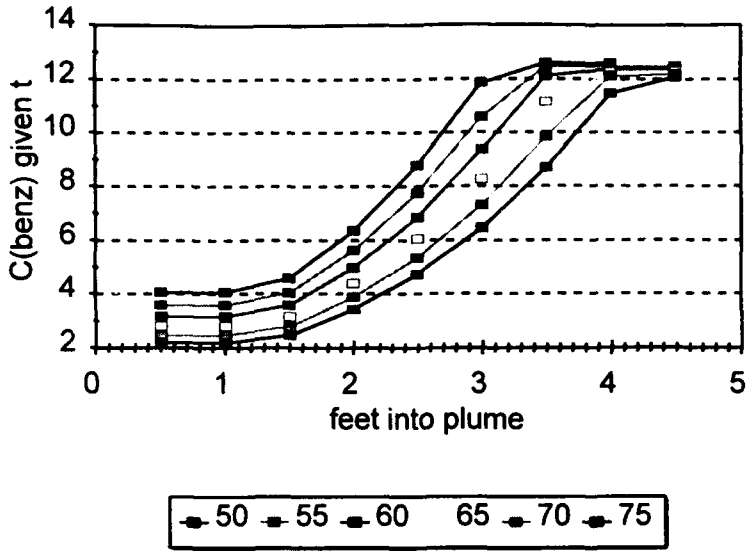

Figure A2-23 C(benz) over Plume Length, @ t = 50 to 75 days, with data:
Vrel = 1.0 ft/d, BTEX = 33, O2 = 4

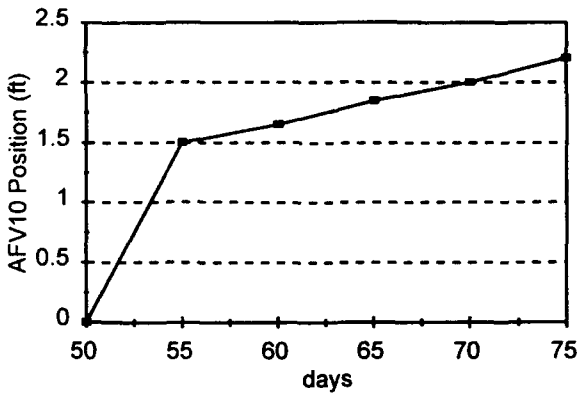

Figure A2-24. AFront Position over time to 75 days with data:
Vrel = 1.0, BTEX = 33, O2 = 4

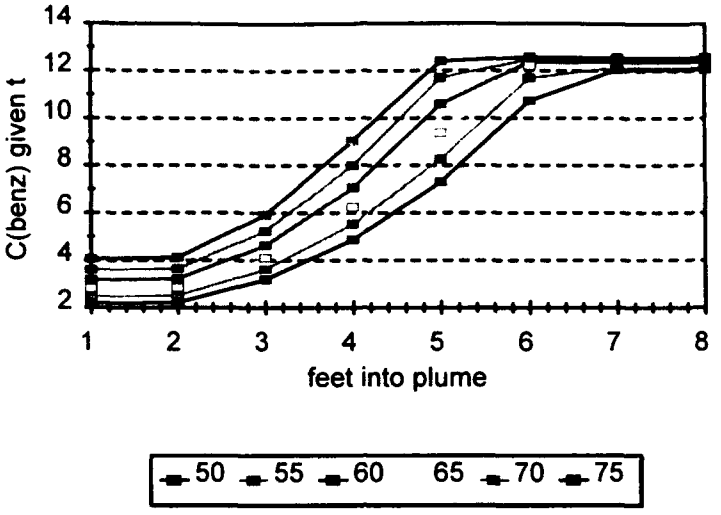

Figure A2-25 C(benz) over Plume Length, @ t = 50 to 75 days, with data:
Vrel = 1.51, BTEX = 33, O2 = 4

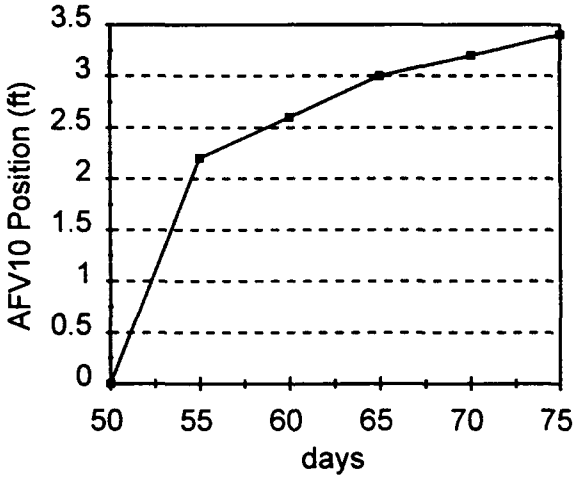

Figure A2-26. AFront Position over time to 75 days with data:
Vrel = 1.51, BTEX = 33, O2 = 4

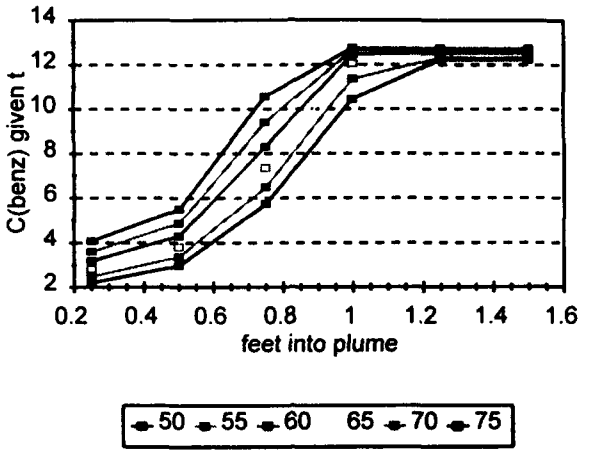

Figure A2-27 C(benz) over Plume Length, @ t = 50 to 75 days, with data: O2 = 2, BTEX = 33, Vrel = 0.5

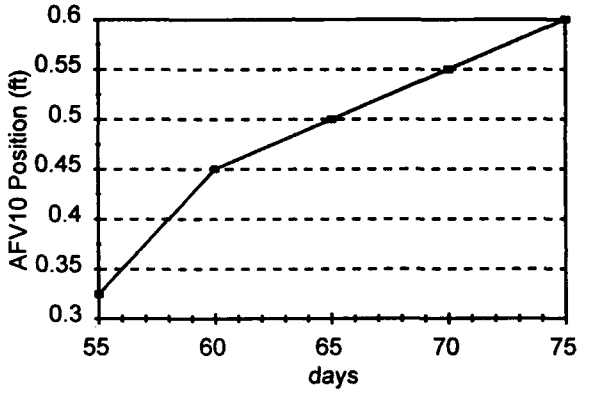

Figure A2-28. AFront Position over time to 75 days with data: O2 = 2, BTEX = 33, Vrel = 0.5

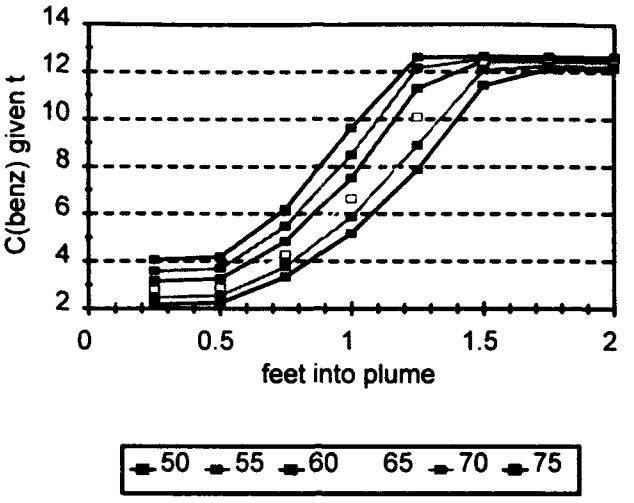

Figure A2-29 C(benz) over Plume Length, @ t = 50 to 75 days, with data: O2 = 3, BTEX = 33, Vrel = 0.5

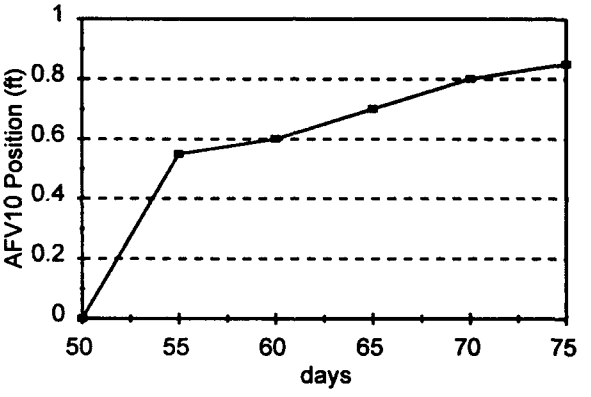

Figure A2-30. AFront Position over time to 75 days with data: O2 = 3, BTEX = 33, Vrel = 0.5

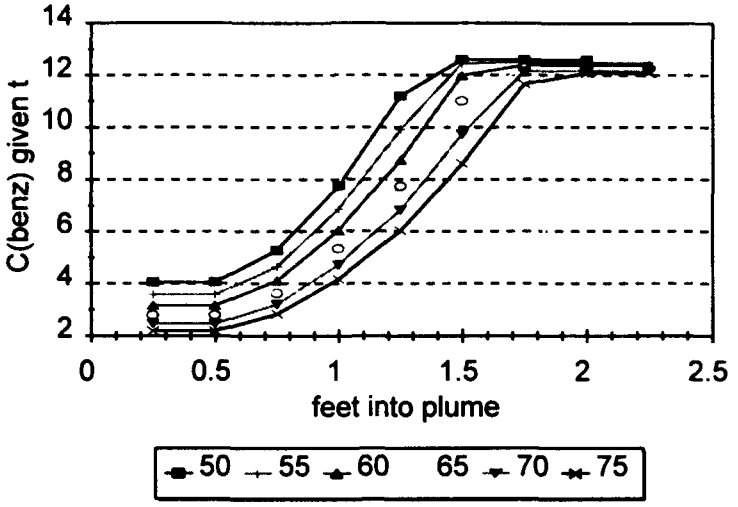

Figure A2-31 C(benz) over Plume Length, @ t = 50 to 75 days, with data:
O2 = 3.5, BTEX = 33, Vrel = 0.5

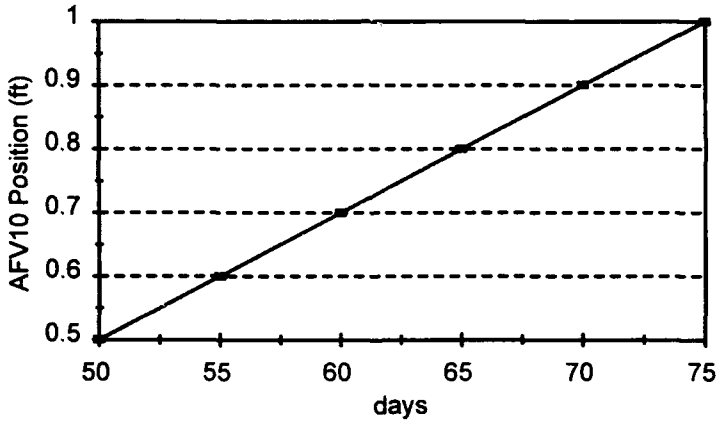

Figure A2-32. AFront Position over time to 75 days with data:
O2 = 3.5, BTEX = 33, Vrel = 0.5

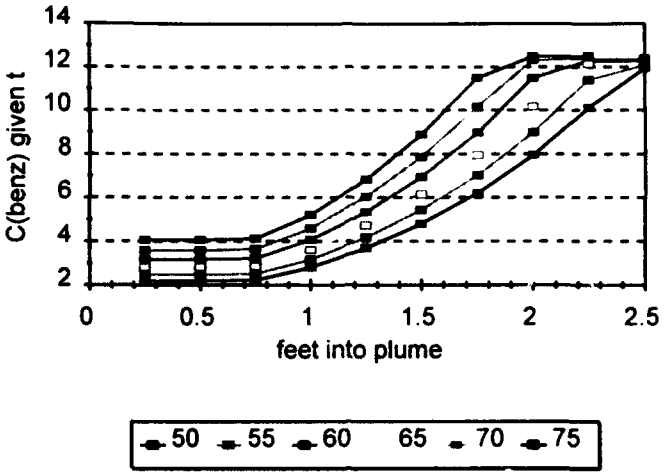

Figure A2-33 C(benz) over Plume Length, @ t = 50 to 75 days, with data: O2 = 5, BTEX = 33, Vrel = 0.5

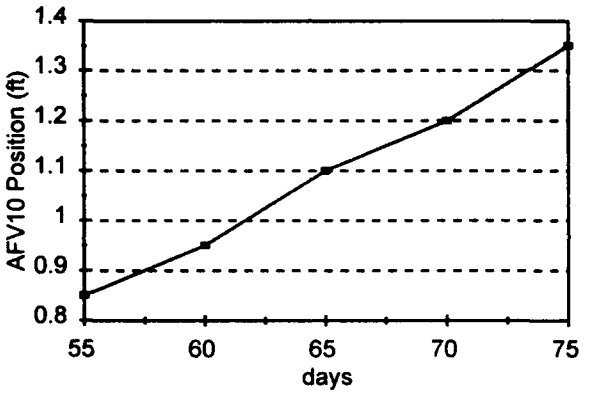

Figure A2-34. AFront Position over time to 75 days with data: O2 = 5, BTEX = 33, Vrel = 0.5

Appendix III. Sample of Dynamic Plume Simulation Model

A. Simulation Model Parameter Input Region

DYNAMIC CASE OF JP-4 DEGRADATION

Initial Values at Site:(mg/l)					Calc: GW/Petrl Velocity		
Benzene	16.40		Hyd Conductivity		V.w	BTEX: R	V.rel
Toluene	16.00		(ft/day)=	18.00		3.927	0.516
EthylB=	2.40		Hy Grad=	0.01	0.69	5.971	0.576
Xylenes'=	5.20	40.00	Porosity=	0.26	ft/d	6.841	0.591
E acceptors (*81%)			organic			14.076	0.643
Oxygen=	2.84		content=	0.0050	V.c		(ft/day)
Nitrate=	16.20		Plm sec=	10.00	0.18	Use:	0.52
MnO2=	4.05		Sec Lth=	1.00			
Fe(OH)3	32.40	75.74	Plume Length			Time stp:	0.500
Sulfate=	20.25		(in ft)=	10.00		(days)	
			Water input ratio:		0.26		

Deg Rate (-k in /days)	Aerobic	EA balance	Anaerob.	EA balance
B	-0.025	1.0003	-0.00167	0.8974
T	-0.040	1.1459	-0.00521	1.0921
E	-0.012	0.8294	-0.00343	1.0116
X	-0.033	1.0847	-0.00357	1.0189

Contam/EA ratio

Cont	O	N	Mn	Fe	S
B	0.325	0.252	0.060	0.024	0.203
T	0.319	0.247	0.059	0.024	0.213
E	0.315	0.244	0.058	0.024	0.221
X	0.315	0.244	0.058	0.024	0.221

B. Simulation Model Display in Section 1 of Plume for Three Time Blocks

DYNAMIC CASE OF JP-4 DEGRADATION

Initial Values at Site:(mg/l)					Calc: GW/Petrl Velocity		
Benzene	16.40		Hyd Conductivity		V.w	BTEX: R	V.rel
Toluene	16.00		(ft/day)=	18.00		3.927	0.516
EthylB=	2.40		Hy Grad=	0.01	0.69	5.971	0.576
Xylenes'=	5.20	40.00	Porosity=	0.26	ft/d	6.841	0.591
E acceptors (*81%)			organic			14.076	0.643
Oxygen=	2.84		content=	0.0050	V.c		(ft/day)
Nitrate=	16.20		Plm sec=	10.00	0.18	Use:	0.52
MnO2=	4.05		Sec Lth=	1.00			
Fe(OH)3	32.40	75.74	Plume Length			Time stp:	0.500
Sulfate=	20.25		(in ft)=	10.00		(days)	
			Water input ratio:		0.26		

Time Blk:	1	Section	1				Section
		P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)
C(Benz):	16.40	16.20	16.20	16.20	16.20	16.20	16.20
C(Tol):	16.00	15.69	15.69	15.69	15.69	15.69	15.69
C(Ethl):	2.40	2.39	2.39	2.39	2.39	2.39	2.39
C(Xyl):	5.20	5.11	5.11	5.11	5.11	5.11	5.11
EAs remaining:		0.92	16.20	4.05	32.40	20.25	0.92
Time Blk:	2	Section	1				Section
		P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)
C(Benz):	16.20	16.01	16.01	16.01	16.01	16.01	16.08
C(Tol):	15.69	15.48	15.47	15.47	15.47	15.47	15.55
C(Ethl):	2.39	2.37	2.37	2.37	2.37	2.37	2.37
C(Xyl):	5.11	5.05	5.05	5.05	5.05	5.05	5.07
EAs remaining:		-0.06	16.13	4.05	32.40	20.25	0.00
Time Blk:	3	Section	1				Section
		P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)	P(O2)
C(Benz):	16.01	15.92	15.91	15.91	15.91	15.91	16.07
C(Tol):	15.47	15.37	15.34	15.34	15.34	15.34	15.53
C(Ethl):	2.37	2.36	2.36	2.36	2.36	2.36	2.37
C(Xyl):	5.05	5.02	5.01	5.01	5.01	5.01	5.07
EAs remaining:		-0.04	15.99	3.96	32.40	20.25	0.00

C. Algorithm Display from Simulation Model: Contaminant (benzene) degradation in section 1, time block 1

Time Blk:	1	Section	1			
		P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
C(Benz):	16.40	16.20	16.20	16.20	16.20	16.20

TS100:A17: 'C(Benz):
TS100:B17: +$TS100:$B$4
TS100:C17: @IF((B17-B17*@EXP($TS100:$H$12*$TS100:$J$5))/$TS100:$J$11>$TS100:$B$9*B17*$TS100:$K$5/@SUM($TS100:$B$4..$B$7),B17-$TS100:$J$11*$TS100:$BS9*B17*$TS100:$K$5/@SUM($TS100:$B$4..$B$7),B17*@EXP($TS100:$HS12*$TS100:$J$5))
TS100:D17: @IF((C17-C17*@EXP(($TS100:$H$12-(@LN(C17/B17)/$TS100:$J$5))*$TS100:$L$5))/$TS100:$K$11>$TS100:$B$10*C17*$TS100:$M$5/@SUM(C17..C20),C17-STS100:$K$11*$TS100:$B$10*C17*$TS100:$M$5/@SUM(C17..C20),C17*@EXP(($TS100:$H$12-(@LN(C17/B17)/$TS100:$J$5))*$TS100:$L$5))
TS100:E17: @IF((D17-D17*@EXP(($TS100:$H$12-(@LN(C17/B17)/$TS100:$J$5)-(@LN(D17/C17)/$TS100:$L$5))*$TS100:$L$5))/$TS100:$L$11>$TS100:$B$11*D17*$TS100:$M$5/@SUM(D17..D20),D17-$TS100:$L$11*$TS100:$B$11*D17*$TS100:$M$5/@SUM(D17..D20),D17*@EXP(($TS100:$H$12-(@LN(C17/B17)/$TS100:$J$5)-(@LN(D17/C17)/$TS100:$L$5))*$TS100:$L$5))
TS100:F17: @IF((E17-E17*@EXP(($TS100:$H$12-(@LN(C17/B17)/$TS100:$J$5)-(@LN(E17/C17)/$TS100:$L$5))*$TS100:$L$5))/$TS100:$M$11>$TS100:$B$12*E17*$TS100:$M$5/@SUM(E17..E20),E17-$TS100:$M$11*$TS100:$B$12*E17*$TS100:$M$5/@SUM(E17..E20),E17*@EXP(($TS100:$H$12-(@LN(C17/B17)/$TS100:$J$5)-(@LN(E17/C17)/$TS100:$L$5))*$TS100:$L$5))
TS100:G17: @IF((F17-F17*@EXP(($TS100:$H$12-(@LN(C17/B17)/$TS100:$J$5)-(@LN(F17/C17)/$TS100:$L$5))*$TS100:$L$5))/$TS100:$N$11>$TS100:$B$13*F17*$TS100:$M$5/@SUM(F17..F20),F17-$TS100:$N$11*$TS100:$B$13*F17*$TS100:$M$5/@SUM(F17..F20),F17*@EXP(($TS100:$H$12-(@LN(C17/B17)/$TS100:$J$5)-(@LN(F17/C17)/$TS100:$L$5))*$TS100:$L$5))

D. Algorithm Display from Simulation Model: Electron acceptor levels after degradation, section 1, time block 1

EAs remaining:	0.92	16.20	4.05	32.40	20.25

TS100:A21: 'EAs remaining:
TS100:C21: +$TS100:$B$9-((B17-C17)/$TS100:$J$11+(B18-C18)/$TS100:$J$12+(B19-C19)/$TS100:$J$13+(B20-C20)/$TS100:$J$14)
TS100:D21: +$TS100:$B$10-((C17-D17)/$TS100:$K$11+(C18-D18)/$TS100:$K$12+(C19-D19)/$TS100:$K$13+(C20-D20)/$TS100:$K$14)
TS100:E21: +$TS100:$B$11-((D17-E17)/$TS100:$L$11+(D18-E18)/$TS100:$L$12+(D19-E19)/$TS100:$L$13+(D20-E20)/$TS100:$L$14)
TS100:F21: +$TS100:$B$12-((E17-F17)/$TS100:$M$11+(E18-F18)/$TS100:$M$12+(E19-F19)/$TS100:$M$13+(E20-F20)/$TS100:$M$14)
TS100:G21: +$TS100:$B$13-((F17-G17)/$TS100:$N$11+(F18-G18)/$TS100:$N$12+(F19-G19)/$TS100:$N$13+(F20-G20)/$TS100:$N$14)

E. Algorithm Display from Simulation Model: Contaminant (benzene and toluene) degradation in section 2 and time block 2

Section	2			
P(O2)	P(NO3)	P(Mn)	P(Fe)	P(SO4)
16.08	16.07	16.06	16.06	16.07

TS100:H24: @IF((L17-L17*@EXP($TS100:$H$12*$TS100:$J$5))/$TS100:$J$11>(C21*$TS100:$F$14+(1-$TS100:$F$14)*H21)*L17*$TS100:$K$5/@SUM(L17..L20),L17-$TS100:$J$11*(C21*$TS100:$F$14+(1-$TS100:$F$14)*H21)*L17*$TS100:$K$5/@SUM(L17..L20),L17*@EXP($TS100:$H$12*$TS100:$J$5))

TS100:I24: @IF((H24-H24*@EXP(($TS100:$H$12-(@LN(H24/L17)/$TS100:$J$5))*$TS100:$L$5))/$TS100:$K$11>(D21*$TS100:$F$14+(1-$TS100:$F$14)*I21)*H24*$TS100:$M$5/@SUM(H24..H27),H24-$TS100:$K$11*(D21*$TS100:$F$14+(1-$TS100:$F$14)*I21)*H24*$TS100:$M$5/@SUM(H24..H27),H24*@EXP(($TS100:$H$12-(@LN(H24/L17)/$TS100:$J$5))*$TS100:$L$5))

TS100:J24: @IF((I24-I24*@EXP(($TS100:$H$12-(@LN(H24/G24)/$TS100:$J$5)-(@LN(I24/H24)/$TS100:$L$5))*$TS100:$L$5))/$TS100:$L$11>($TS100:$F$10*$TS100:$F$14*O21/$TS100:$H$10+(1-$TS100:$F$10*$TS100:$F$14/$TS100:$H$10)*J21)*I24*$TS100:$M$5/@SUM(I24..I27),I24-$TS100:$L$11*($TS100:$F$10*$TS100:$F$14*O21/$TS100:$H$10+(1-$TS100:$F$10*$TS100:$F$14/$TS100:$H$10)*J21)*I24*$TS100:$M$5/@SUM(I24..I27),I24*@EXP(($TS100:$H$12-(@LN(H24/G24)/$TS100:$J$5)-(@LN(I24/H24)/$TS100:$L$5))*$TS100:$L$5))

TS100:K24: @IF((J24-J24*@EXP(($TS100:$H$12-(@LN(H24/G24)/$TS100:$J$5)-(@LN(J24/H24)/$TS100:$L$5))*$TS100:$L$5))/$TS100:$M$11>($TS100:$F$10*$TS100:$F$14*P21/$TS100:$H$10+(1-$TS100:$F$10*$TS100:$F$14/$TS100:$H$10)*K21)*J24*$TS100:$M$5/@SUM(J24..J27),J24-$TS100:$M$11*($TS100:$F$10*$TS100:$F$14*P21/$TS100:$H$10+(1-$TS100:$F$10*$TS100:$F$14/$TS100:$H$10)*K21)*J24*$TS100:$M$5/@SUM(J24..J27),J24*@EXP(($TS100:$H$12-(@LN(H24/G24)/$TS100:$J$5)-(@LN(J24/H24)/$TS100:$L$5))*$TS100:$L$5))

TS100:L24: @IF((K24-K24*@EXP(($TS100:$H$12-(@LN(H24/L17)/$TS100:$J$5)-(@LN(K24/H24)/$TS100:$L$5))*$TS100:$L$5))/$TS100:$N$11>(G21*$TS100:$F$14+(1-$TS100:$F$14)*L21)*K24*$TS100:$M$5/@SUM(K24..K27),K24-$TS100:$N$11*(G21*$TS100:$F$14+(1-$TS100:$F$14)*L21)*K24*$TS100:$M$5/@SUM(K24..K27),K24*@EXP(($TS100:$H$12-(@LN(H24/L17)/$TS100:$J$5)-(@LN(K24/H24)/$TS100:$L$5))*$TS100:$L$5))

Vita

Captain John T. Enyeart was born on 16 March 1967 in Pullman, Washington. He graduated from Goldendale High School in Goldendale, Washington in 1985. He attended Washington State University in Pullman, Washington where he earned a Bachelor of Science degree in General Studies-Physical Sciences in May 1989. As a member of the Reserve Officer Training Corps, he was commissioned into the United States Air Force upon graduation. While awaiting assignment, Captain Enyeart remained at Pullman and earned a Bachelor of Science degree in Agricultural Engineering in December 1989.

Captain Enyeart was initially assigned to the 842nd Civil Engineering Squadron, Grand Forks AFB, North Dakota as a Design Engineer. He later became a Programming Engineer and then Chief of the Readiness Branch. In April 1992, Captain Enyeart was assigned as the Environmental Coordinator in the 8th Civil Engineering Squadron, Kunsan AB, Republic of Korea. He entered the Engineering and Environmental Management Program, School of Engineering, Air Force Institute of Technology in May 1993. Upon graduation in September 1994, he will be assigned to the Air Force Center for Environmental Excellence, Brooks AFB, Texas.

Captain Enyeart is married to the former Elisabeth A. Allen of San Antonio, Texas.

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13. ABSTRACT *(Maximum 200 words)*

This research evaluated the process of intrinsic bioremediation, also called natural attenuation, and the parameters that affected it. The goal of this study was to use these intrinsic bioremediation parameters to develop a valid prediction of the cleanup duration using this restoration technology. This analysis was limited to a JP-4 release and focused on the remediation of the BTEX constituents to a cleanup level of 10 ppm total BTEX. Of the many factors that affect intrinsic bioremediation, those that most influenced its occurrence were the quantities of aerobic and anaerobic electron acceptors used in biodegradation. The electron acceptors considered in this research were oxygen, nitrate, manganese (IV), iron (III), and sulfate. A no-dispersion biodegradation model was developed to determine the prediction of the intrinsic bioremediation duration based on the concentrations of individual electron acceptors. Only the aerobic electron acceptor had a measurable influence on the biodegradation model; hence, the prediction results focused on the aerobic biodegradation and its boundary with the anaerobic portion. A linear regression was performed to relate BTEX, oxygen and the relative velocity of ground water through the plume to the motion of this aerobic boundary. With future validation of this regression data, this information may be used by Air Force site managers to predict the time aerobic intrinsic bioremediation can restore a plume of a given size.

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